Aluminium-mediated Aromatic C–F Bond Activation: Regioswitchable Construction of Benzene-fused Triphenylene Frameworks

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Supporting Information

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1. General Statement

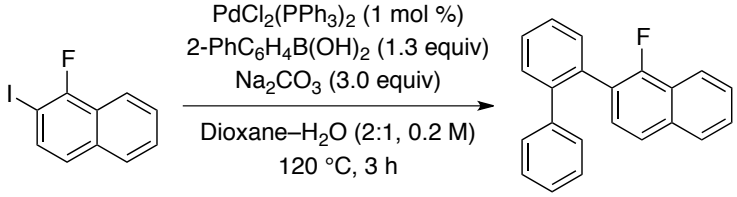
^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance 500 or a JEOL ECS-400 spectrometer. Chemical shift values are given in ppm relative to internal Me_4Si (for ^{1}H NMR: δ = 0.00 ppm), $CDCl_3$ (for ^{13}C NMR: δ = 77.0 ppm) and C_6F_6 (for ^{19}F NMR: δ = 0.00 ppm). IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR) method. Mass spectra were measured on a JEOL JMS-T100GCV or a JMS-T100CS spectrometer. Elemental analyses were carried out at the Elemental Analysis Laboratory, Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba.

Column chromatography and preparative thin-layer chromatography (PTLC) were conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography and Wakogel B-5F, Wako Pure Chemical Industries for PTLC). All the reactions were conducted under nitrogen. Diethyl ether, tetrahydrofuran (THF) and dichloromethane were purified by a solvent-purification system (GlassContour) equipped with columns of activated alumina and supported-copper catalyst (Q-5) before use. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) and chlorobenzene were distilled from CaH_2 and stored over activated molecular sieves 4A. 1-Fluoro-2-iodonaphthalene (**4a**)[1], 1-chloronaphthalen-2-yl trifluoromethanesulfonate[2] and 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate[3] were prepared according to the literature procedures. Unless otherwise noted, materials were obtained from commercial sources and used directly without further purifications.

2. Preparation of Cyclisation Precursors 1

2.1 Preparation of 1-Fluoronaphthalenes 1a–1f

2-(Biphenyl-2-yl)-1-fluoronaphthalene (1a)



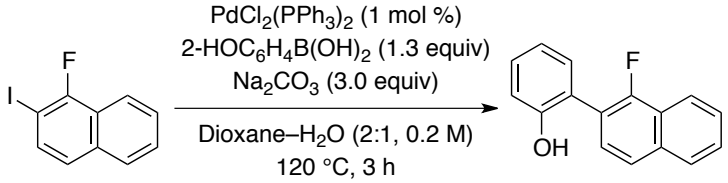
4a **1a**

In a flask were placed 1-fluoro-2-iodonaphthalene (**4a**, 2.72 g, 10.0 mmol), (biphenyl-2-yl)boronic acid (2.57 g, 13.0 mmol), Na_2CO_3 (3.18 g, 30.0 mmol), and $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol). After the flask was purged with nitrogen, a degassed mixture of 1,4-dioxane (33.3 mL) and water (16.7 mL) was added. The mixture was heated at 120 °C for 3 h, and then cooled to room temperature. After aqueous HCl (2 M, 30 mL) was added to the reaction mixture, the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to give **1a** (2.97 g, quant.) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (dd, *J* = 8.4, 7.3 Hz, 1H), 7.14–7.16 (m, 3H), 7.17–7.19 (m,

2H), 7.44–7.53 (m, 7H), 7.77–7.79 (m, 1H), 8.02–8.03 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 120.8 (d, J = 6 Hz), 122.8 (d, J = 3 Hz), 123.3 (d, J = 15 Hz), 123.7 (d, J = 17 Hz), 126.2, 126.60, 126.60, 127.2, 127.4, 127.9, 128.2, 129.0 (d, J = 3 Hz), 129.3, 130.4, 131.4, 133.9 (d, J = 3 Hz), 134.4, 141.2, 141.7, 154.9 (d, J = 253 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 35.6 (d, J_{FH} = 7 Hz, 1F). IR (neat): ν 3059, 3020, 1483, 1464, 1377, 814, 760, 741, 700 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{22}H_{15}F$ $[M]^+$: 298.1158; Found: 298.1165.

2-(1-Fluoronaphthalen-2-yl)phenol

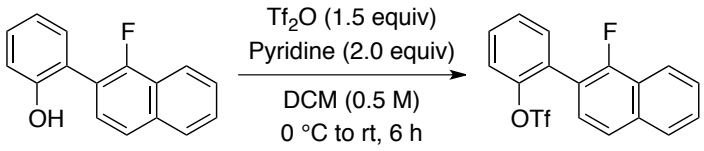


4a

In a flask were placed 1-fluoro-2-iodonaphthalene (**4a**, 5.44 g, 20.0 mmol), (2-hydroxyphenyl)boronic acid (3.59 g, 26.0 mmol), Na_2CO_3 (6.36 g, 60.0 mmol), and $PdCl_2(PPh_3)_2$ (140 mg, 0.20 mmol). After the flask was purged with nitrogen, a degassed mixture of 1,4-dioxane (66.7 mL) and water (33.3 mL) was added. The mixture was heated at 120 °C for 3 h, and then cooled to room tempurture. After aqueous HCl (2 M, 30 mL) was added to the reaction mixture, the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 15:1) to give 2-(1-fluoronaphthalen-2-yl)phenol (4.76 g, quant.) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.99 (brs, 1H), 7.04–7.08 (m, 2H), 7.33–7.36 (m, 2H), 7.46 (dd, J = 8.4 Hz, J_{HF} = 7.2 Hz, 1H), 7.57–7.63 (m, 2H), 7.75 (d, J = 8.5 Hz, 1H), 7.90–7.92 (m, 1H), 8.17–8.19 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 116.1, 118.3 (d, J_{CF} = 15 Hz), 120.79, 120.84, 122.4, 123.8 (d, J_{CF} = 17 Hz), 124.2, 126.7, 127.2, 127.4 (d, J_{CF} = 3 Hz), 128.1 (d, J_{CF} = 4 Hz), 129.7, 131.2, 134.5 (d, J_{CF} = 5 Hz), 152.9, 155.2 (d, J = 253 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 37.8 (d, J_{FH} = 7 Hz, 1F). IR (neat): ν 3537, 3423, 3059, 1448, 1379, 1282, 1176, 1049, 889, 808, 783, 748, 715, 667, 602, 565 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{16}H_{11}FO$ $[M]^+$: 238.0794; Found: 238.0802.

2-(1-Fluoronaphthalen-2-yl)phenyl trifluoromethanesulfonate (5)

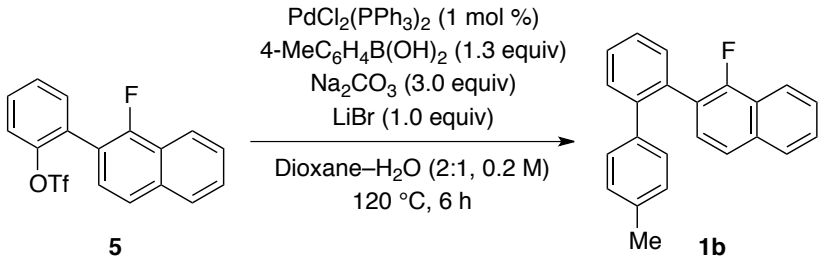


5

To a dichloromethane (40 mL) solution of 2-(1-fluoronaphthalen-2-yl)phenol (4.77 g, 20.0 mmol) and pyridine (3.22 mL, 39.8 mmol) was added Tf_2O (5.05 mL, 30.0 mmol) dropwise at 0 °C. After stirring at 0 °C for 5 min, the mixture was warmed to room temperature and stirred for

another 6 h. After water (40 mL) was added to the reaction mixture, the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 25:1) to give **5** (7.33 g, 99%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (dd, J = 8.5 Hz, J_{HF} = 7.2 Hz, 1H), 7.45–7.48 (m, 1H), 7.49–7.54 (m, 2H), 7.56–7.58 (m, 1H), 7.59–7.61 (m, 2H), 7.73 (d, J = 8.5 Hz, 1H), 7.90–7.92 (m, 1H), 8.17–8.19 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 117.2 (d, J_{CF} = 14 Hz), 118.3 (q, J_{CF} = 322 Hz), 121.0 (d, J_{CF} = 6 Hz), 121.9, 123.5 (d, J_{CF} = 17 Hz), 123.7 (d, J_{CF} = 4 Hz), 126.8, 127.49, 127.51, 127.6 (d, J_{CF} = 2 Hz), 128.4, 129.76, 129.80 (d, J_{CF} = 12 Hz), 132.7, 134.8 (d, J_{CF} = 5 Hz), 147.3, 155.3 (d, J_{CF} = 256 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 37.8 (d, J_{FH} = 7 Hz, 1F), 87.6 (s, 3F). IR (neat): ν 3068, 1495, 1421, 1383, 1248, 1209, 1138, 1080, 1049, 903, 877, 852, 816, 768, 598 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{17}H_{10}F_4O_3S$ $[M]^+$: 370.0287; Found: 370.0282.

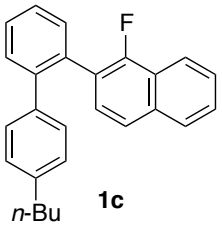
1-Fluoro-2-(4'-methylbiphenyl-2-yl)naphthalene (1b)



5 **1b**

In a Schlenk tube were placed 2-(1-fluoronaphthalen-2-yl)phenyl trifluoromethanesulfonate (**5**, 222 mg, 0.600 mmol), (4-methylphenyl)boronic acid (106 mg, 0.78 mmol), Na_2CO_3 (191 mg, 1.8 mmol), LiBr (52 mg, 0.60 mmol), and $PdCl_2(PPh_3)_2$ (4.2 mg, 6 μmol). After the tube was purged with nitrogen, a degassed mixture of 1,4-dioxane (2.0 mL) and water (1.0 mL) was added. The mixture was heated at 120 °C for 6 h, and then cooled to room tempurture. After aqueous HCl (2 M, 3 mL) was added to the reaction mixture, the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to give **1b** (173 mg, 92%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.24 (s, 3H), 6.96 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 7.11 (dd, J = 8.3 Hz, J_{HF} = 7.2 Hz, 1H), 7.42–7.53 (m, 7H), 7.78–7.80 (m, 1H), 8.03–8.05 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.0, 120.8 (d, J = 6 Hz), 122.8, 123.4 (d, J = 14 Hz), 123.7 (d, J = 17 Hz), 126.2, 126.5, 126.9, 127.3, 128.1, 128.6, 129.1, 130.4, 131.4, 133.87, 133.89, 134.3, 136.2, 138.3, 141.7, 154.9 (d, J = 252 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 35.5 (d, J_{FH} = 7 Hz, 1F). IR (neat): ν 3055, 3022, 2918, 1487, 1464, 1377, 814, 758, 729, 710 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{23}H_{17}F$ $[M]^+$: 312.1314; Found: 312.1320.

2-(4'-Butylbiphenyl-2-yl)-1-fluoronaphthalene (1c)

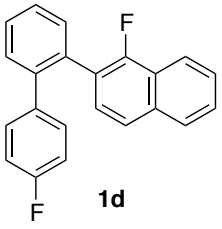


1c

1-Fluoronaphthalene **1c** was prepared by the method described for **1b** using 2-(1-fluoronaphthalen-2-yl)phenyl trifluoromethanesulfonate (**5**, 222 mg, 0.600 mmol), (4-butylphenyl)boronic acid (139 mg, 0.78 mmol), Na_2CO_3 (191 mg, 1.8 mmol), LiBr (52 mg, 0.60 mmol), and $PdCl_2(PPh_3)_2$ (4.2 mg, 6 μmol). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) gave **1c** (167 mg, 78%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, J = 7.4 Hz, 3H), 1.23–1.30 (m, 2H), 1.48–1.54 (m, 2H), 2.50 (t, J = 7.7 Hz, 2H), 6.95 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 7.11 (dd, J = 8.3, J_{HF} = 7.4 Hz, 1H), 7.41–7.51 (m, 7H), 7.77–7.80 (m, 1H), 8.02–8.04 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.9, 22.3, 33.3, 35.2, 120.8 (d, J_{CF} = 6 Hz), 122.7 (d, J_{CF} = 5 Hz), 123.4 (d, J_{CF} = 15 Hz), 123.7 (d, J_{CF} = 17 Hz), 126.1 (d, J_{CF} = 2 Hz), 126.5, 126.9, 127.3 (d, J_{CF} = 3 Hz), 127.9, 128.1, 129.1, 129.2 (d, J_{CF} = 4 Hz), 130.4, 131.4, 133.9 (d, J_{CF} = 5 Hz), 134.4, 138.4, 141.2, 141.8, 154.9 (d, J_{CF} = 253 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 35.6 (d, J_{FH} = 7 Hz, 1F). IR (neat): ν 3055, 2954, 2927, 2856, 1604, 1487, 1464, 1377, 1259, 1192, 1059, 814, 760, 744, 602, 565 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{26}H_{23}F$ $[M]^+$: 354.1784; Found: 354.1768.

1-Fluoro-2-(4'-fluorobiphenyl-2-yl)naphthalene (1d)



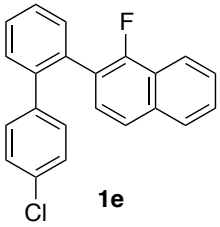
1d

1-Fluoronaphthalene **1d** was prepared by the method described for **1b** using 2-(1-fluoronaphthalen-2-yl)phenyl trifluoromethanesulfonate (**5**, 222 mg, 0.600 mmol), (4-fluorophenyl)boronic acid (109 mg, 0.78 mmol), Na_2CO_3 (191 mg, 1.8 mmol), LiBr (52 mg, 0.60 mmol), and $PdCl_2(PPh_3)_2$ (4.2 mg, 6 μmol). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) gave **1d** (174 mg, 92%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.84 (dd, J = 8.7 Hz, J_{HF} = 7.9 Hz, 2H), 7.10–7.15 (m, 3H), 7.44–7.53 (m, 7H), 7.79–7.81 (m, 1H), 8.01–8.03 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 114.8 (d, J_{CF} = 21 Hz), 120.8 (d, J_{CF} = 6 Hz), 122.99 (d, J_{CF} = 14 Hz), 123.01 (d, J_{CF} = 4 Hz), 123.6 (d, J_{CF} = 17 Hz), 126.3 (d, J_{CF} = 1 Hz), 126.7, 127.3, 127.4 (d, J_{CF} = 3 Hz), 128.2, 128.8 (d, J_{CF} = 4 Hz), 130.2, 130.8 (d, J_{CF} = 8 Hz), 131.4, 134.0 (d, J_{CF} = 5 Hz), 134.5, 137.2 (d, J_{CF} = 3 Hz), 140.7, 154.8 (d, J_{CF} = 252 Hz), 161.7 (d, J_{CF} = 247 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 35.9 (d, J_{FH} = 8 Hz, 1F), 45.58–45.64 (m, 1F). IR (neat): ν 3060, 3020, 1604, 1514, 1487, 1466, 1377, 1223, 1159, 1057, 837, 814,

760, 744 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{22}H_{14}F_2$ $[M]^+$: 316.1064; Found: 316.1068.

2-(4'-Chlorobiphenyl-2-yl)-1-fluoronaphthalene (1e)

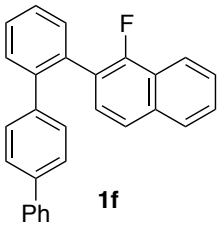


1e

1-Fluoronaphthalene **1e** was prepared by the method described for **1b** using 2-(1-fluoronaphthalen-2-yl)phenyl trifluoromethanesulfonate (**5**, 222 mg, 0.600 mmol), (4-chlorophenyl)boronic acid (122 mg, 0.78 mmol), Na_2CO_3 (191 mg, 1.8 mmol), LiBr (52 mg, 0.60 mmol), and $PdCl_2(PPh_3)_2$ (4.2 mg, 6 μmol). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) gave **1e** (180 mg, 90%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09–7.13 (m, 5H), 7.45–7.53 (m, 7H), 7.79–7.81 (m, 1H), 8.01–8.03 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 120.8 (d, J_{CF} = 6 Hz), 122.8 (d, J_{CF} = 15 Hz), 123.1 (d, J_{CF} = 4 Hz), 123.6 (d, J_{CF} = 17 Hz), 126.4, 126.8, 127.4 (d, J_{CF} = 3 Hz), 127.5, 128.1, 128.3, 128.8 (d, J_{CF} = 4 Hz), 130.2, 130.5, 131.5, 132.7, 134.0 (d, J_{CF} = 5 Hz), 134.4, 139.7, 140.5, 154.8 (d, J_{CF} = 252 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 35.9 (d, J_{FH} = 7 Hz, 1F). IR (neat): ν 3060, 3020, 1604, 1514, 1487, 1466, 1377, 1223, 1159, 1157, 837, 814, 760, 744 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{22}H_{14}ClF$ $[M]^+$: 332.0768; Found: 332.0770.

1-Fluoro-2-(1,1':4',1''-terphenyl-2-yl)naphthalene (1f)



1f

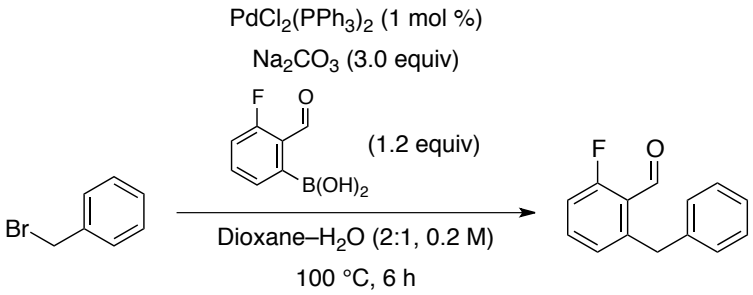
1-Fluoronaphthalene **1f** was prepared by the method described for **1b** using 2-(1-fluoronaphthalen-2-yl)phenyl trifluoromethanesulfonate (**5**, 222 mg, 0.600 mmol), (biphenyl-4-yl)boronic acid (155 mg, 0.78 mmol), Na_2CO_3 (191 mg, 1.8 mmol), LiBr (52 mg, 0.60 mmol), and $PdCl_2(PPh_3)_2$ (4.2 mg, 6 μmol). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) gave **1f** (207 mg, 92%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (dd, J = 8.4 Hz, J_{HF} = 7.3 Hz, 1H), 7.24–7.30 (m, 2H), 7.36–7.41 (m, 4H), 7.45–7.57 (m, 10H), 7.78–7.80 (m, 1H), 8.03–8.05 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 120.8 (d, J_{CF} = 6 Hz), 123.0 (d, J_{CF} = 4 Hz), 123.2 (d, J_{CF} = 15 Hz), 123.7 (d, J_{CF} = 17 Hz), 126.3, 126.55, 126.64, 126.9, 127.17, 127.23, 127.4 (d, J_{CF} = 3 Hz), 128.2, 128.7, 129.1 (d, J_{CF} = 4 Hz), 129.7, 130.4, 131.5, 134.0 (d, J_{CF} = 5 Hz), 134.4, 139.2, 140.2, 140.6, 141.3, 154.9 (d, J_{CF} = 252 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 35.6 (d, J_{FH} = 7 Hz, 1F). IR (neat): ν 3057, 3028, 1603, 1483, 1464, 1377, 1257, 1061, 1007, 908, 841, 816, 752, 729, 698, 565 cm^{-1}. HRMS (EI+): *m*/*z*

Calcd. for $C_{28}H_{19}F$ $[M]^+$: 374.1471; Found: 374.1478.

2.2 Preparation of 1-Fluoroanthracene 1g

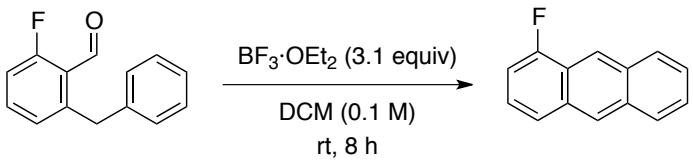
2-Benzyl-6-fluorobenzaldehyde



In a flask were placed benzyl bromide (0.299 mL, 2.51 mmol), (3-fluoro-2-formylphenyl)boronic acid (504 mg, 3.00 mmol), Na_2CO_3 (795 mg, 7.50 mmol), and $PdCl_2(PPh_3)_2$ (18 mg, 25 μmol). After the flask was purged with nitrogen, a degassed mixture of 1,4-dioxane (8.3 mL) and water (4.2 mL) was added. The mixture was heated at 100 °C for 6 h, and then cooled to room tempurture. After saturated aqueous NH_4Cl (15 mL) was added to the reaction mixture, the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to give 2-benzyl-6-fluorobenzaldehyde (398 mg, 74%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.43 (s, 2H), 7.00 (d, J = 7.9 Hz, 1H), 7.06 (dd, J_{HF} = 10.7 Hz, J = 8.3 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.28 (dd, J = 8.1, 7.4 Hz, 2H), 7.47 (ddd, J = 8.3, 7.9 Hz, J_{HF} = 5.9 Hz, 1H), 10.52 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 38.6, 114.4 (d, J_{CF} = 21 Hz), 126.3, 127.3 (d, J_{CF} = 4 Hz), 128.4, 128.6 (d, J_{CF} = 15 Hz), 129.0, 135.1 (d, J_{CF} = 12 Hz), 139.7, 144.8, 166.4 (d, J_{CF} = 248 Hz), 188.9 (d, J_{CF} = 11 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 41.0 (dd, J_{FH} = 11, 6 Hz, 1F). IR (neat): ν 3030, 2791, 1697, 1612, 1572, 1471, 1456, 1417, 1254, 1186, 822, 785, 725, 700 cm^{-1}. HRMS (EI+): *m/z* Calcd. for $C_{14}H_{11}FO$ $[M]^+$: 214.0794; Found: 214.0803.

1-Fluoroanthracene[4]

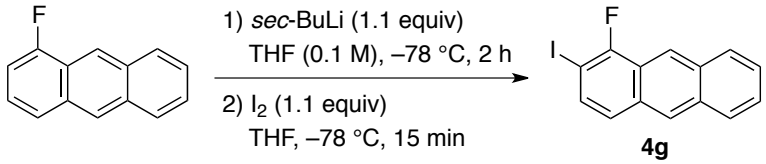


To a dichloromethane (15.0 mL) solution of 2-benzyl-6-fluorobenzaldehyde (321 mg, 1.50 mmol) was added $BF_3{\cdot}OEt_2$ (0.565 mL, 4.58 mmol) at room temperature. After stirring at room temperature for 8 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The organic materials were extracted with CH_2Cl_2 thrice, and the combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by

silica gel column chromatography (hexane) to give 1-fluoroanthracene (244 mg, 83%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (dd, J_{HF} = 10.9 Hz, J = 7.4 Hz, 1H), 7.37 (ddd, J = 8.6, 7.4 Hz, J_{HF} = 5.3 Hz, 1H), 7.49–7.52 (m, 2H), 7.79 (d, J = 8.6 Hz, 1H), 7.99–8.02 (m, 1H), 8.04–8.07 (m, 1H), 8.45 (s, 1H), 8.68 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 107.6 (d, J_{CF} = 20 Hz), 119.6 (d, J_{CF} = 4 Hz), 122.9 (d, J_{CF} = 17 Hz), 124.0 (d, J_{CF} = 4 Hz), 124.6 (d, J_{CF} = 8 Hz), 125.9, 126.07, 126.10 (d, J_{CF} = 4 Hz), 128.1, 128.6, 131.6, 131.1, 132.7 (d, J_{CF} = 4 Hz), 158.9 (d, J_{CF} = 253 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 39.2 (dd, J_{FH} = 11, 5 Hz, 1F). IR (neat): ν 3060, 3043, 1639, 1556, 1537, 1460, 1313, 1250, 1200, 1134, 889, 789, 744, 729 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{14}H_9F$ $[M]^+$: 196.0688; Found: 196.0695.

1-Fluoro-2-iodonaphthalene (4g)

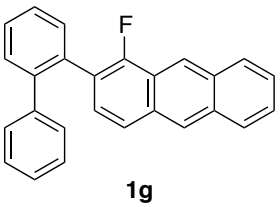


4g

To a THF (12 mL) solution of 1-fluoroanthracene (236 mg, 1.20 mmol) was added *sec*-BuLi (1.03 M in hexane, 1.28 mL, 1.32 mmol) at –78 °C. After stirring at –78 °C for 2 h, a THF (1.3 mL) solution of I_2 (335 mg, 1.32 mmol) was added to the reaction mixture. The mixture was stirred at –78 °C for another 15 min, and then warmed to room temperature. The reaction was quenched with saturated aqueous $NaHCO_3$, and the organic materials were extracted with ether thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane) to give **4g** (377 mg, 97%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51–7.56 (m, 3H), 7.62 (dd, J = 9.0, J_{HF} = 5.9 Hz, 1H), 7.98–8.00 (m, 1H), 8.04–8.06 (m, 1H), 8.41 (s, 1H), 8.62 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 74.1 (d, J_{CF} = 25 Hz), 119.3 (d, J_{CF} = 3 Hz), 122.6 (d, J_{CF} = 19 Hz), 125.3 (d, J_{CF} = 5 Hz), 126.35 (d, J_{CF} = 3 Hz), 126.42, 126.5, 128.1, 128.7, 131.8, 132.0 (d, J_{CF} = 4 Hz), 132.3, 133.1, 158.5 (d, J_{CF} = 252 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 61.0 (d, J_{FH} = 6 Hz, 1F). IR (neat): ν 3049, 1620, 1574, 1533, 1454, 1360, 1309, 1192, 1136, 881, 742, 731 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{14}H_8FI$ $[M]^+$: 321.9655; Found: 321.9660.

2-(Biphenyl-2-yl)-1-fluoroanthracene (1g)

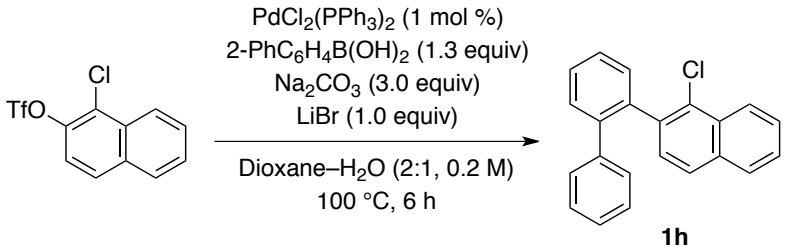


1g

1-Fluoroanthracene **1g** was prepared by the method described for **1a** using 1-fluoro-2-iodonaphthalene (**4g**, 193 mg, 0.60 mmol), (biphenyl-2-yl)boronic acid (154 mg, 0.78 mmol), Na_2CO_3 (191 mg, 1.8 mmol), and $PdCl_2(PPh_3)_2$ (4.2 mg, 6 μmol). Purification by silica gel column chromatography (hexane/EtOAc = 40:1) gave **1g** (149 mg, 71%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (dd, J = 8.8 Hz, J_{HF} = 7.3 Hz, 1H), 7.13–7.15 (m, 3H), 7.21–7.23 (m, 2H), 7.46–7.54 (m, 5H), 7.58–7.61 (m, 2H), 7.97–7.99 (m, 1H), 8.00–8.02 (m, 1H), 8.36 (s, 1H), 8.60 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 119.8 (d, J_{CF} = 5 Hz), 121.4 (d, J_{CF} = 15 Hz), 122.9 (d, J_{CF} = 18 Hz), 123.1 (d, J_{CF} = 5 Hz), 125.85, 125.89 (d, J_{CF} = 3 Hz), 126.0, 126.7, 127.2, 127.9, 128.1, 128.2, 128.49, 128.52, 129.3, 130.4, 131.4, 131.7, 131.9 (d, J_{CF} = 2 Hz), 131.1, 134.4, 141.2, 141.8, 154.7 (d, J_{CF} = 254 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 36.3 (d, J_{FH} = 7 Hz). IR (neat): ν 3053, 2924, 2852, 1460, 1430, 1362, 1323, 881, 742, 700 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{26}H_{17}F$ $[M]^+$: 348.1314; Found: 348.1331.

2.3 Preparation of 1-Halonaphthalenes 1h–1j

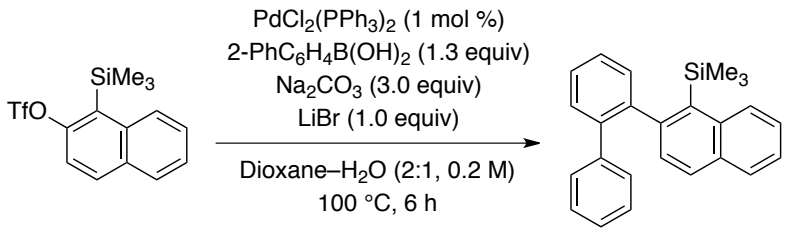
2-(Biphenyl-2-yl)-1-chloronaphthalene (1h)



1h

In a flask were placed 1-chloronaphthalen-2-yl trifluoromethanesulfonate (311 mg, 1.00 mmol), (biphenyl-2-yl)boronic acid (257 mg, 1.30 mmol), Na_2CO_3 (318 mg, 3.00 mmol), LiBr (87 mg, 1.0 mmol), and $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol). After the flask was purged with nitrogen, a degassed mixture of 1,4-dioxane (3.33 mL) and water (1.67 mL) was added to the flask. The mixture was heated at 100 °C for 6 h, and then cooled to room tempurture. After saturated aqueous NH_4Cl (10 mL) was added to the reaction mixture, the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to give **1h** (274 mg, 87%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10–7.18 (m, 6H), 7.42–7.47 (m, 2H), 7.49–7.53 (m, 3H), 7.57–7.60 (m, 2H), 7.79 (d, J = 8.1 Hz, 1H), 8.30 (d, J = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 124.8, 126.1, 126.4, 126.6, 126.9, 127.1, 127.8, 128.0, 128.1, 129.1, 129.2, 130.1, 130.4, 131.0, 131.1, 133.4, 137.9, 138.6, 141.0, 141.3. IR (neat): ν 3055, 3022, 1481, 1458, 1331, 1252, 974, 818, 741, 700, 538 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{22}H_{15}Cl$ $[M]^+$: 314.0862; Found: 314.0863.

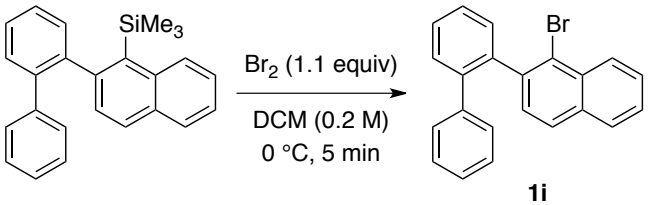
[2-(Biphenyl-2-yl)naphthalen-1-yl]trimethylsilane



In a flask were placed 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate (2.44 g, 7.00 mmol), 2-biphenylboronic acid (1.80 g, 9.09 mmol), Na_2CO_3 (2.23 g, 21.0 mmol), LiBr (608 mg, 7.00 mol), and $PdCl_2(PPh_3)_2$ (49 mg, 0.070 mmol). After the flask was purged with nitrogen, a degassed mixture of 1,4-dioxane (23.3 mL) and water (11.7 mL) was added. The mixture was heated at 100 °C for 6 h, and then cooled to room tempurture. After saturated aqueous NH_4Cl (40 mL) was added to the reaction mixture, the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to give [2-(biphenyl-2-yl)naphthalen-1-yl]trimethylsilane (2.30 g, 93%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.12 (s, 9H), 7.01 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.12–7.13 (m, 2H), 7.18–7.20 (m, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 6.6 Hz, 1H), 7.42–7.50 (m, 4H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 2.3, 124.9, 125.1, 126.5, 126.6, 127.8, 127.9, 128.5, 128.6, 128.9, 129.7, 129.8, 130.1, 132.1, 132.2, 135.6, 137.5, 140.0, 140.9, 143.5, 147.7. IR (neat): ν 3055, 2954, 2895, 1481, 1252, 854, 837, 766, 741, 700 cm^{-1}. HRMS (EI+): *m/z* Calcd. for $C_{25}H_{24}Si$ $[M]^+$: 352.1647; Found: 352.1646.

2-(Biphenyl-2-yl)-1-bromonaphthalene (1i)



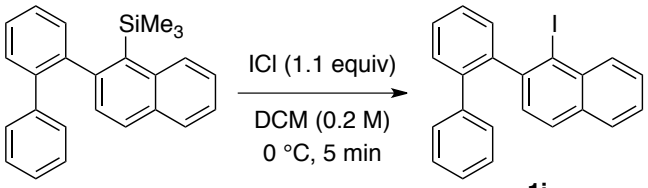
1i

To a dichloromethane (10 mL) solution of [2-(biphenyl-2-yl)naphthalen-1-yl]trimethylsilane (705 mg, 2.00 mmol) was added bromine (113 μL, 2.2 mmol) at 0 °C. After stirring at 0 °C for 5 min, the reaction was quenched with saturated aqueous $Na_2S_2O_3$, and the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to give **1i** (635 mg, 88%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09–7.13 (m, 4H), 7.17–7.20 (m, 2H), 7.39–7.50 (m, 5H), 7.56–7.60 (m, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 8.32 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 123.7, 126.4, 126.6, 126.8, 126.9, 127.4, 127.7, 127.8, 128.07, 128.11, 129.2, 129.3, 130.1, 131.1,

132.3, 133.3, 140.60, 140.64, 140.9, 141.0. IR (neat): ν 3055, 3020, 1481, 1323, 957, 818, 760, 741, 700 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{22}H_{15}{}^{79}Br$ $[M]^+$: 358.0357; Found: 358.0341.

2-(Biphenyl-2-yl)-1-iodonaphthalene (1j)



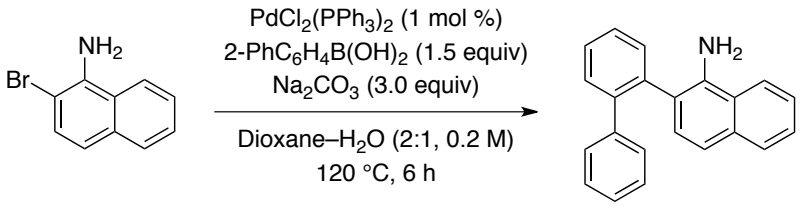
1j

To a dichloromethane (5.0 mL) solution of [2-(biphenyl-2-yl)naphthalen-1-yl]trimethylsilane (705 mg, 2.00 mmol) was added a dichloromethane (5.0 mL) solution of ICl (357 mg, 2.20 mmol) at 0 °C. After stirring at 0 °C for 5 min, the reaction was quenched with saturated aqueous $Na_2S_2O_3$, and the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to give **1j** (699 mg, 86%) as a white solid.

^1H NMR (500 MHz, $CDCl_3$): δ 7.09–7.17 (m, 4H), 7.20–7.22 (m, 2H), 7.35 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.43–7.58 (m, 5H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 105.6, 126.4, 126.6, 126.9, 127.7, 127.8, 127.9, 128.18, 128.21, 128.5, 129.5, 130.2, 131.3, 132.6, 133.1, 134.9, 140.6, 140.8, 144.2, 145.9. IR (neat): ν 3055, 3016, 1481, 1448, 1313, 947, 818, 762, 742, 700 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{22}H_{15}I$ $[M]^+$: 406.0218; Found: 406.0221.

2.4. Preparation of 1-Aminonaphthalene 1k

2-(Biphenyl-2-yl)naphthalen-1-amine (1k)



1k

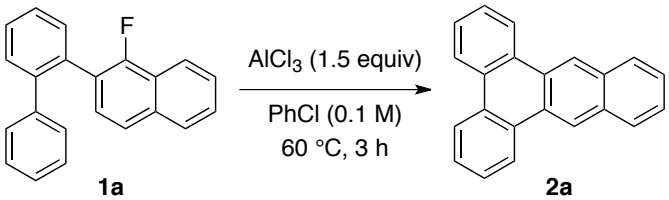
In a flask were placed 2-bromonaphthalen-1-amine (1.11 g, 5.00 mmol), biphenyl-2-ylboronic acid (1.48 g, 7.50 mmol), Na_2CO_3 (1.59 g, 15.0 mmol), and $PdCl_2(PPh_3)_2$ (35 mg, 0.050 mmol). After the flask was purged with nitrogen, a degassed mixture of 1,4-dioxane (16.7 mL) and water (8.3 mL) was added to the flask. The mixture was heated at 120 °C for 6 h and then cooled to room temperature. After saturated aqueous NH_4Cl was added to the reaction mixture, the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 7:1) to give **1k** (1.34 g, 91%) as a

pale purple solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05 (d, *J* = 8.3 Hz, 1H), 7.12–7.14 (m, 3H), 7.19–7.22 (m, 3H), 7.42–7.44 (m, 2H), 7.46–7.50 (m, 3H), 7.54 (d, *J* = 6.9 Hz, 1H), 7.74–7.76 (m, 1H), 7.79–7.80 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 118.2, 121.0, 121.8, 123.5, 124.9, 125.5, 126.7, 127.8, 127.9, 128.0, 128.4, 129.0, 129.2, 130.7, 131.5, 133.5, 137.9, 138.5, 141.0, 141.8. IR (neat): ν 3473, 3384, 3055, 3020, 1614, 1398, 804, 764, 740, 700 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{22}H_{17}N$ $[M]^+$: 295.1361; Found: 295.1373.

3. $AlCl_3$-Mediated Cyclisation of 1-Fluoronaphthalenes 1

Benzo[*f*]tetraphene (2a)

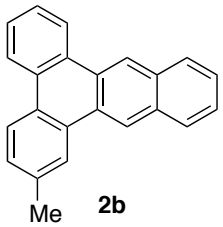


1a **2a**

In a Schlenk tube were placed 2-(biphenyl-2-yl)-1-fluoronaphthalene (**1a**, 30 mg, 0.10 mmol) and $AlCl_3$ (20 mg, 0.15 mmol). After the tube was purged with nitrogen, chlorobenzene (1.0 mL) was added. The mixture was heated at 60 °C for 3 h, and then cooled to room temperature. After aqueous NaOH (1 M, 5 mL) was added to the reaction mixture, the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to give **2a** (28 mg, 99%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.60–7.65 (m, 4H), 8.05 (dd, *J* = 6.4, 3.3 Hz, 2H), 8.55 (d, *J* = 7.9 Hz, 2H), 8.74 (d, *J* = 7.9 Hz, 2H), 9.03 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.0, 123.4, 123.6, 126.1, 127.4, 127.6, 128.1, 128.4, 130.0, 130.1, 132.2. IR (neat): ν 3735, 2927, 1684, 1506, 773, 669 cm^{-1}. HRMS (APCI+): *m*/*z* Calcd. for $C_{22}H_{14}$ $[M]^+$: 278.1096; Found: 293.1090.

2-Methylbenzo[*f*]tetraphene (2b)



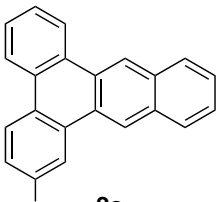
2b

Benzo[*f*]tetraphene **2b** was synthesised by the method described for **2a** using 1-fluoronaphthalene **1b** (63 mg, 0.20 mmol) and $AlCl_3$ (40 mg, 0.30 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 20:1) gave **2b** (55 mg, 94%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.63 (s, 3H), 7.46 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.54–7.58 (m, 2H),

7.61–7.65 (m, 2H), 8.07–8.10 (m, 2H), 8.46 (d, J = 8.3 Hz, 1H), 8.53–8.55 (m, 1H), 8.56 (brs, 1H), 8.74–8.78 (m, 1H), 9.07 (s, 1H), 9.07 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.8, 121.9, 122.0, 123.2, 123.4, 123.6, 123.8, 126.00, 126.01, 127.0, 127.6, 127.7, 128.07, 128.08, 128.4, 128.6, 129.0, 129.8, 130.1, 130.2, 132.17, 132.20, 137.2. IR (neat): ν 3053, 2914, 2854, 1616, 1516, 1491, 1439, 1346, 1242, 879, 814, 762, 717, 692 cm^{-1}. HRMS (APCI+): m/z Calcd. for $C_{23}H_{17}$ $[M+H]^+$: 293.1330; Found: 293.1322.

2-Butylbenzo[*f*]tetraphene (2c)

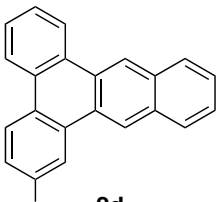


2c

Benzo[*f*]tetraphene **2c** was synthesised by the method described for **2a** using 1-fluoronaphthalene **1c** (71 mg, 0.20 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and HFIP (2.0 mL). Purification by silica gel column chromatography (hexane/EtOAc = 20:1) gave **2c** (63 mg, 94%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (t, J = 7.5 Hz, 3H), 1.48 (tq, J = 7.8, 7.5 Hz, 2H), 1.79 (tt, J = 7.8, 7.8 Hz, 2H), 2.89 (t, J = 7.8 Hz, 2H), 7.48 (dd, J = 8.3, 1.7 Hz, 1H), 7.54–7.57 (m, 2H), 7.61–7.64 (m, 2H), 8.07–8.11 (m, 2H), 8.48 (d, J = 8.4 Hz, 1H), 8.53–8.55 (m, 2H), 8.74–8.76 (m, 1H), 9.07 (s, 1H), 9.08 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.0, 22.5, 33.8, 36.0, 121.9, 122.0, 123.21, 123.21, 123.4, 123.6, 125.97, 125.99, 127.0, 127.6, 127.9, 128.05, 128.09, 128.3, 128.5, 128.6, 129.8, 130.0, 130.2, 132.15, 132.19, 142.2. IR (neat): ν 3053, 2954, 2927, 2856, 1614, 1491, 1454, 1412, 876, 764, 719 cm^{-1}. HRMS (APCI+): m/z Calcd. for $C_{26}H_{23}$ $[M+H]^+$: 335.1800; Found: 335.1806.

2-Fluorobenzo[*f*]tetraphene (2d)



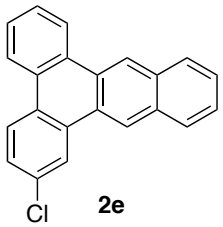
2d

Benzo[*f*]tetraphene **2d** was synthesised by the method described for **2a** using 1-fluoronaphthalene **1d** (63 mg, 0.20 mmol) and $AlCl_3$ (40 mg, 0.30 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 20:1) gave **2d** (57 mg, 96%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (ddd, J_{HF} = 10.6 Hz, J = 8.5, 2.5 Hz, 1H), 7.55–7.59 (m, 2H), 7.60–7.65 (m, 2H), 8.05–8.07 (m, 2H), 8.33 (dd, J = 11.0 Hz, J_{HF} = 2.5 Hz, 1H), 8.44–8.46 (m, 1H), 8.50 (dd, J = 8.5 Hz, J_{HF} = 5.9 Hz, 1H), 8.71–8.72 (m, 1H), 8.89 (s, 1H), 9.02 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 109.3 (d, J_{CF} = 23 Hz), 115.5 (d, J_{CF} = 23 Hz), 122.2, 122.4, 123.2, 123.7, 125.6 (d, J_{CF} = 9 Hz), 126.3, 126.4, 126.5 (d, J_{CF} = 3 Hz), 127.3, 127.6 (d, J = 3 Hz), 127.7, 128.07,

128.11, 128.5, 129.5, 129.6, 132.1, 132.2 (d, J_{CF} = 7 Hz), 132.5, 162.4 (d, J_{CF} = 246 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 47.56–47.61 (m, 1F). IR (neat): ν 3051, 1616, 1516, 1493, 1462, 1279, 1213, 1188, 876, 856, 764 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{22}H_{13}F$ $[M]^+$: 296.1001; Found: 296.0999.

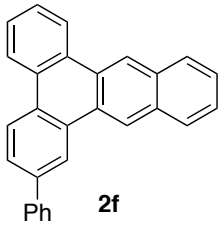
2-Chlorobenzo[*f*]tetraphene (2e)



2e

Benzo[*f*]tetraphene **2e** was synthesised by the method described for **2a** using 1-fluoronaphthalene **1e** (67 mg, 0.20 mmol) and $AlCl_3$ (40 mg, 0.30 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 20:1) gave **2e** (60 mg, 95%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53–7.60 (m, 3H), 7.61–7.66 (m, 2H), 8.02–8.08 (m, 2H), 8.42 (d, *J* = 8.8 Hz, 1H), 8,45 (d, *J* = 7.7 Hz, 1H), 8.62 (d, *J* = 1.7 Hz, 1H), 8.69 (d, *J* = 7.7 Hz, 1H), 8.89 (s, 1H), 8.98 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.1, 122.3, 123.3, 123.4, 123.7, 124.9, 126.3, 126.4, 127.2, 127.66, 127.70, 127.71, 128.06, 128.13, 128.38, 128.45, 129.2, 130.0, 131.6, 132.1, 132.5, 133.5. IR (neat): ν 3053, 2924, 1730, 1599, 1506, 1487, 1431, 1103, 876, 762, 715, 690 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{22}H_{14}Cl$ $[M+H]^+$: 313.0784; Found: 313.0792.

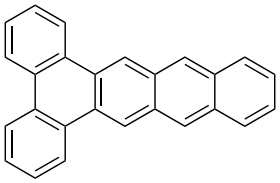
2-Phenylbenzo[*f*]tetraphene (2f)



2f

Benzo[*f*]tetraphene **2f** was synthesised by the method described for **2a** using 1-fluoronaphthalene **1f** (75 mg, 0.20 mmol) and $AlCl_3$ (40 mg, 0.30 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 20:1) gave **2d** (65 mg, 91%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (t, *J* = 7.6 Hz, 1H), 7.55–7.58 (m, 3H), 7.66–7.74 (m, 3H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.88 (d, *J* = 8.6 Hz, 1H), 8.07–8.13 (m, 2H), 8.59–8.61 (m, 1H), 8.64 (d, *J* = 8.6 Hz, 1H), 8.78–8.79 (m, 1H), 8.95 (brs, 1H), 9.10 (s, 1H), 9.15 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.1, 122.17, 122.23, 123.5, 123.7, 124.0, 126.16, 126.17, 126.7, 127.4, 127.5, 127.6, 127.7, 128.10, 128.11, 128.5, 128.6, 129.0, 129.2, 129.9, 130.1, 130.4, 132.2, 132.3, 140.2, 141.2. IR (neat): ν 3051, 3030, 1485, 872, 756, 715, 692 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{28}H_{19}$ $[M+H]^+$: 355.1487; Found: 355.1482.

Dibenzo[*a*,*c*]tetracene (2g)



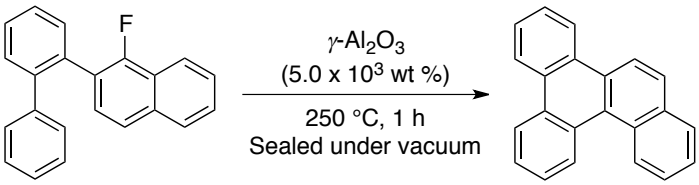
2g

Dibenzo[*a*,*c*]tetraphene (**2g**) was synthesised by the method described for **2a** using 1-fluoronaphthalene **1c** (70 mg, 0.20 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and HFIP (2.0 mL). Purification by silica gel column chromatography (hexane/EtOAc = 20:1) gave **2g** (63 mg, 96%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.62–7.67 (m, 4H), 8.07 (dd, *J* = 6.3, 2.8 Hz, 2H), 8.53 (d, *J* = 7.6 Hz, 2H), 8.69 (s, 2H), 8.78 (d, *J* = 8.5 Hz, 2H), 9.24 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.0, 123.4, 123.7, 125.3, 126.3, 127.6, 127.8, 128.2, 128.4, 130.2, 130.3, 130.5, 131.9. IR (neat): ν 2918, 2854, 1722, 1431, 1279, 891, 746, 729 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{26}H_{16}$ $[M]^+$: 328.1252; Found: 328.1244.

4. γ-Al_2O_3-Cyclisation of 1-Fluoronaphthalenes 1

Benzo[*g*]chrysene (3a)

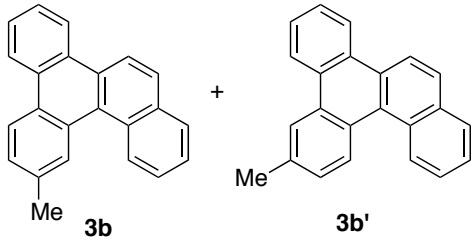


1a **3a**

γ-Al_2O_3 (1.00 g) was activated by annealing at 500 °C for 30 min under vacuum (~10^{-2} mbar) in a glass ampule. To the ampule was added **1a** (20 mg, 0.067 mmol) under argon atmosphere, and the mixture was shaken for 2–3 min. The ampule was then evacuated (~10^{-2} mbar) and sealed. The mixture was heated at 250 °C for 1 h, and then cooled to room temperature. The reaction mixture was filtered through a glass filter (dichloromethane), and the filtrate was concentrated under reduced pressure to give **3a** (18 mg, 95%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58–7.72 (m, 6H), 7.99–8.02 (m, 2H), 8.61 (d, *J* = 8.9 Hz, 1H), 8.65–8.67 (m, 1H), 8.70–8.72 (m, 1H), 8.74 (d, *J* = 8.1 Hz, 1H), 8.91 (d, *J* = 8.2 Hz, 1H), 8.95 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 120.7, 123.0, 123.4, 123.7, 125.8, 125.9, 126.0, 126.6, 127.0, 127.21, 127.24, 127.6, 128.0, 128.1, 128.4, 129.3, 129.4, 129.7, 129.9, 130.1, 130.8, 133.5. IR (neat): ν 3055, 1493, 1479, 1450, 818, 758, 723 cm^{-1}. HRMS (APCI+): *m*/*z* Calcd. for $C_{22}H_{14}$ $[M]^+$: 278.1096; Found: 278.1083.

12-Methylbenzo[*g*]chrysene (3b) and 13-Methylbenzo[*g*]chrysene (3b')



3b **3b'**

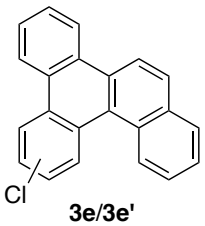
A mixture of benzo[*g*]chrysenes **3b** and **3b'** was synthesised by the method described for **3a** using 1-fluoronaphthalene **1b** (20 mg, 0.064 mmol) and γ-Al_2O_3 (1.00 g). The reaction mixture was filtered through a glass filter (dichloromethane), and the filtrate was concentrated under reduced pressure to give a mixture of **3b** and **3b'** (14 mg, 73%, 64:36) as a white solid.

3b + **3b'**: IR (neat): ν 3053, 2916, 2854, 1610, 1498, 1473, 1444, 1379, 1244, 906, 812, 789, 758, 725 cm^{-1}. HRMS (APCI+): *m*/*z* Calcd. for $C_{23}H_{17}$ $[M+H]^+$: 293.1330; Found: 293.1318.

3b: ^1H NMR (500 MHz, $CDCl_3$): δ 2.61 (s, 3H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.57–7.70 (m, 4H), 7.96–8.02 (m, 2H), 8.60 (d, *J* = 8.9 Hz, 1H), 8.61–8.71 (m, 4H), 8.96 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.8, 120.8, 122.9, 123.4, 123.7, 125.7, 125.9, 126.9, 127.1, 127.2, 127.5, 128.10, 128.10, 128.12, 128.4, 128.6, 129.2, 129.4, 129.5, 130.0, 130.3, 133.5, 135.8.

3b': ^1H NMR (500 MHz, $CDCl_3$): δ 2.65 (s, 3H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.57–7.70 (m, 4H), 7.96–8.02 (m, 2H), 8.53 (s, 1H), 8.59–8.71 (m, 3H), 8.79 (d, *J* = 8.4 Hz, 1H), 8.93 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.8, 120.8, 123.1, 123.4, 123.7, 125.77, 125.83, 127.0, 127.18, 127.20, 127.3, 127.4, 127.5, 127.6, 128.1, 128.4, 129.3, 129.8, 129.9, 130.2, 130.9, 133.5, 136.4.

Chlorobenzo[*g*]chrysenes 3e and 3e'



3e/3e'

A mixture of benzo[*g*]chrysenes **3e** and **3e'** was synthesised by the method described for **3a** using 1-fluoronaphthalene **1e** (20 mg, 0.060 mmol) and γ-Al_2O_3 (1.00 g). The reaction mixture was filtered through a glass filter (dichloromethane), and the filtrate was concentrated under reduced pressure to give a mixture of **3e** and **3e'** (14 mg, 75%, 75:25) as a white solid.

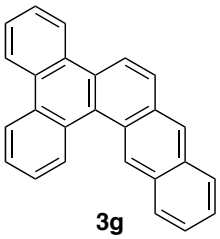
3e + **3e'**: IR (neat): ν 3059, 2922, 2850, 1714, 1595, 1489, 1473, 1439, 1265, 1095, 810, 762, 719 cm^{-1}. HRMS (APCI+): *m*/*z* Calcd. for $C_{22}H_{14}Cl$ $[M+H]^+$: 313.0784; Found: 313.0773.

3e: ^1H NMR (500 MHz, $CDCl_3$): δ 7.56–7.74 (m, 5H), 7.99–8.02 (m, 2H), 8.56–8.66 (m, 4H), 8.86 (d, *J* = 5.3 Hz, 1H), 8.87 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 120.6, 123.0, 123.8, 125.1, 126.08, 126.12, 126.5, 126.8, 127.4, 127.6, 127.8, 128.27, 128.34, 128.5, 128.6, 129.2, 129.4, 129.7, 130.0, 130.7, 132.2, 133.5.

3e': ^1H NMR (500 MHz, $CDCl_3$): δ 7.56–7.74 (m, 5H), 7.99–8.02 (m, 2H), 8.56–8.66 (m, 4H), 8.80

(d, J = 8.9 Hz, 1H), 8.82 (d, J = 8.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 120.7, 123.16, 123.17, 123.8, 126.0, 126.2, 126.3, 126.7, 127.3, 127.8, 127.9, 127.96, 128.04, 128.1, 128.2, 128.9, 130.0, 130.1, 130.8, 132.2, 132.6, 133.6.

Dibenzo[*a*,*c*]tetraphene (3g)

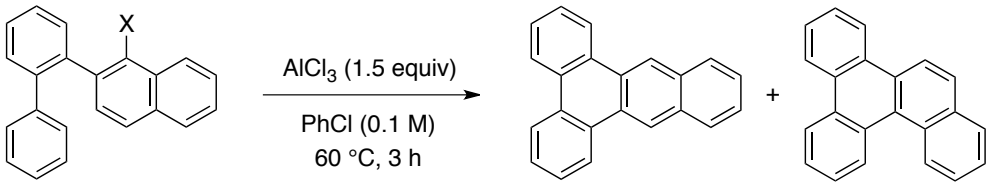


3g

Dibenzo[*a*,*c*]tetraphene (**3g**) was synthesised by the method described for **3a** using 1-fluoroanthracene **1g** (20 mg, 0.057 mmol) and γ-Al_2O_3 (1.00 g). The reaction mixture was filtered through a glass filter (dichloromethane), and the filtrate was concentrated under reduced pressure to give **3g** (13.8 mg, 73%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53–7.58 (m, 2H), 7.69–7.75 (m, 4H), 8.08–8.11 (m, 3H), 8.52 (s, 1H), 8.54 (d, J = 9.2 Hz, 1H), 8.64–8.67 (m, 1H), 8.74–8.77 (m, 1H), 8.79 (dd, J = 7.8, 1.7 Hz, 1H), 9.08 (dd, J = 7.7, 1.5 Hz, 1H), 9.48 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 120.9, 123.1, 123.5, 123.8, 125.6, 125.9, 126.0, 126.3, 126.5, 127.0, 127.1, 127.3, 127.5, 127.8, 127.9, 128.1, 128.5, 128.7, 129.0, 129.6, 129.7, 130.1, 130.9, 131.4, 131.7, 131.8. IR (neat): ν 3053, 2927, 2850, 1496, 1433, 906, 885, 754, 739 cm^{-1}. HRMS (APCI+): m/z Calcd. for $C_{26}H_{16}$ $[M]^+$: 328.1252; Found: 328.1243.

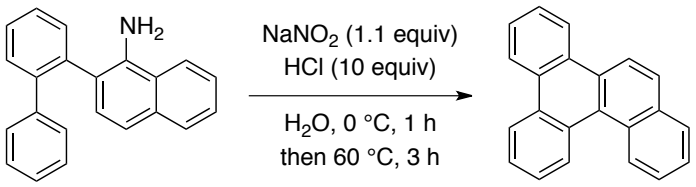
5. Mechanistic Study 1: $AlCl_3$-Mediated Cyclisation of Halonaphthalenes 1h–1j



1h–1j **2a** **3a**

In a Schlenk tube were placed 2-(biphenyl-2-yl)-1-halonaphthalene **1h**, **1i**, or **1j** (0.10 mmol) and $AlCl_3$ (20 mg, 0.15 mmol). After the tube was purged with nitrogen, chlorobenzene (1.0 mL) was added. The mixture was heated at 60 °C for 3 h, and then cooled to room temperature. After aqueous NaOH (1 M, 5 mL) was added to the reaction mixture, the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the yields of **2a** and **3a** were determined by ^{1}H NMR measurement using CH_2Br_2 as an internal standard.

6. Mechanistic Study 2: Cyclisation of Diazonium Salt



1k **3a**

In a two-necked flask were placed 2-(biphenyl-2-yl)naphthalen-1-amine (**1k**, 295 mg, 1.00 mmol) and aqueous HCl (2 M, 5.0 mL, 10 mmol) at 0 °C. After stirring at 0 °C for 15 min, $NaNO_2$ (76 mg, 1.1 mmol) was added. After stirring for another 1 h, the mixture was heated at 60 °C for 3 h, and then cooled to room temperature. After saturated aqueous $NaHCO_3$ was added to the reaction mixture, the organic materials were extracted with dichloromethane thrice. The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 25:1) to give **3a** (250 mg, 90%) as a white solid.

7. References

(1) T. Rausis and M. Schlosser, *Eur. J. Org. Chem.*, 2002, 3351–3358.

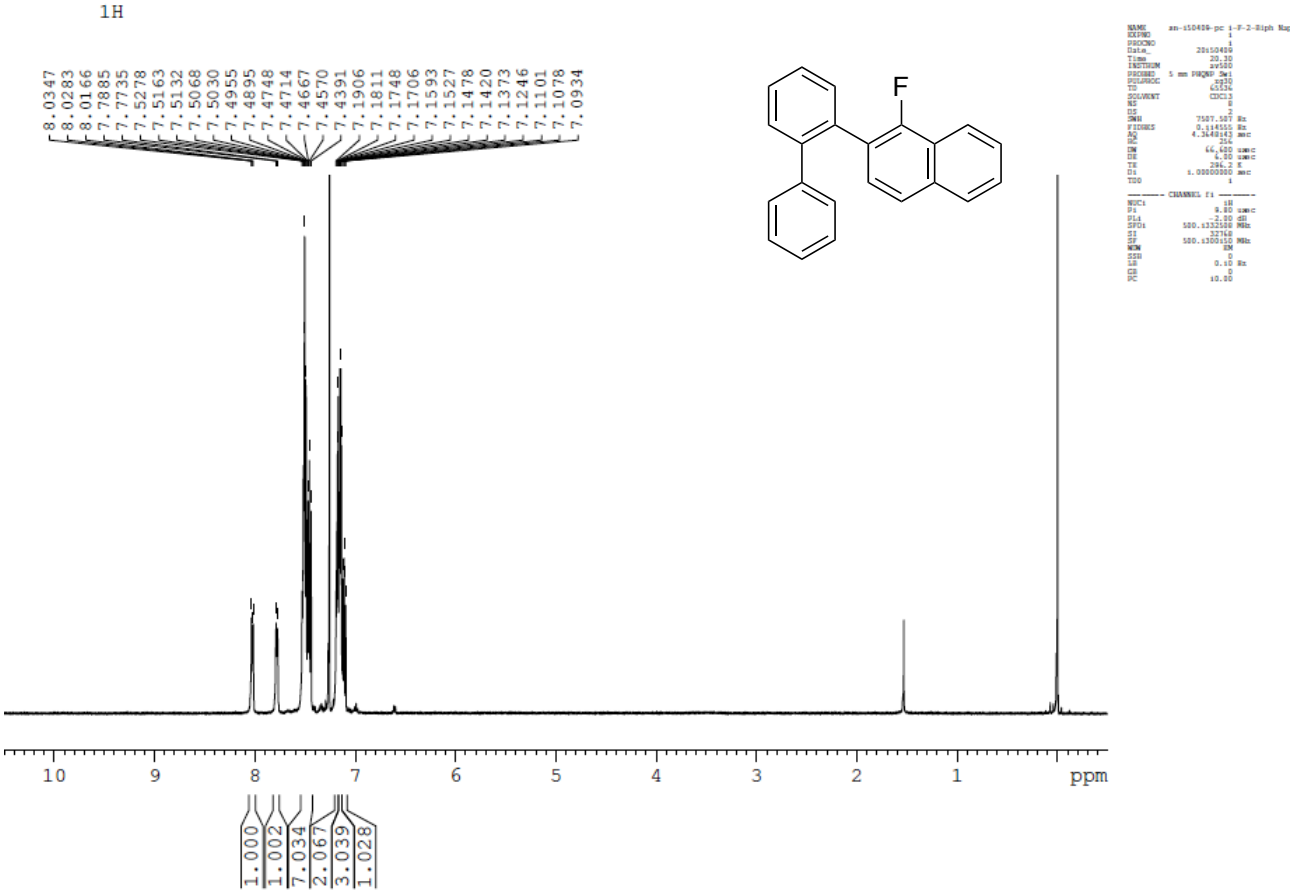
(2) J. Barluenga, A. Jiménez-Aquino, F. Aznar and C. Valdés, *J. Am. Chem. Soc.*, 2009, **131**, 4031–4041.

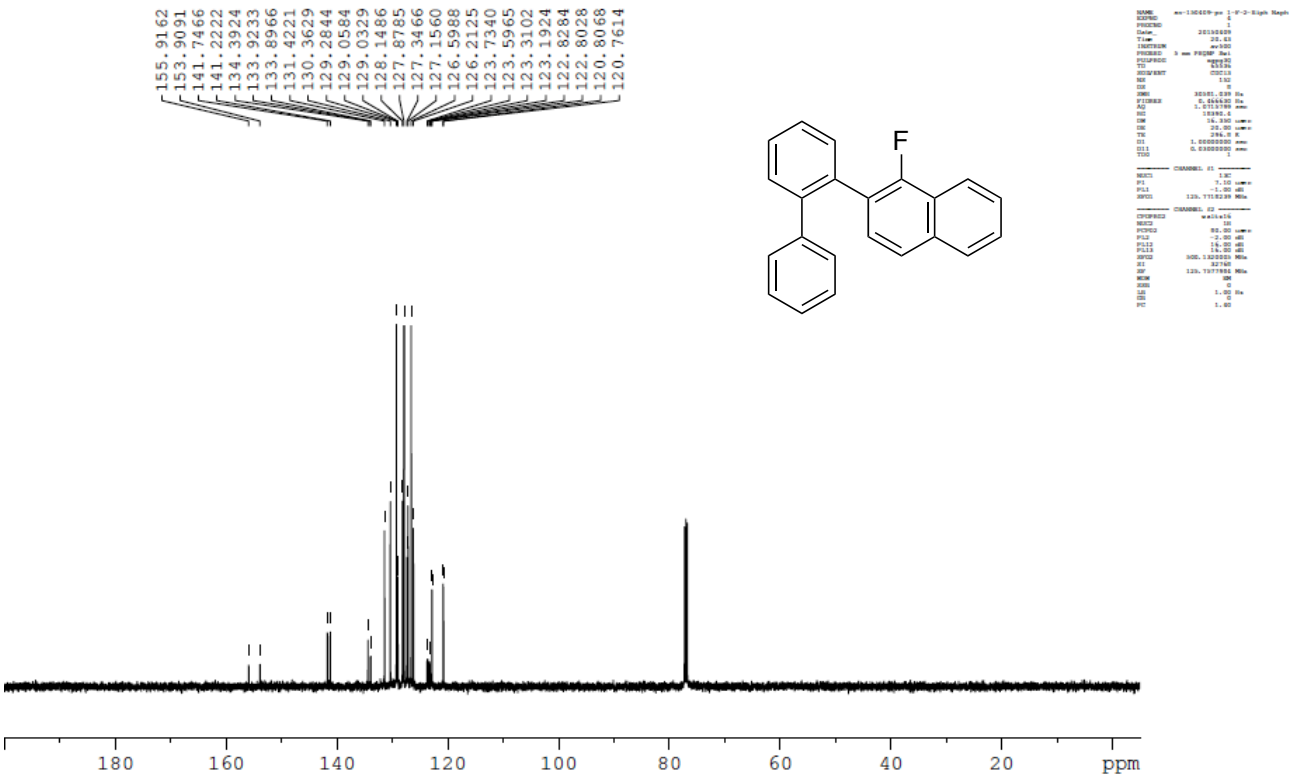
(3) D. Peña, A. Cobas, D. Pérez and E. Guitián, *Synthesis*, 2002, 1454–1458.

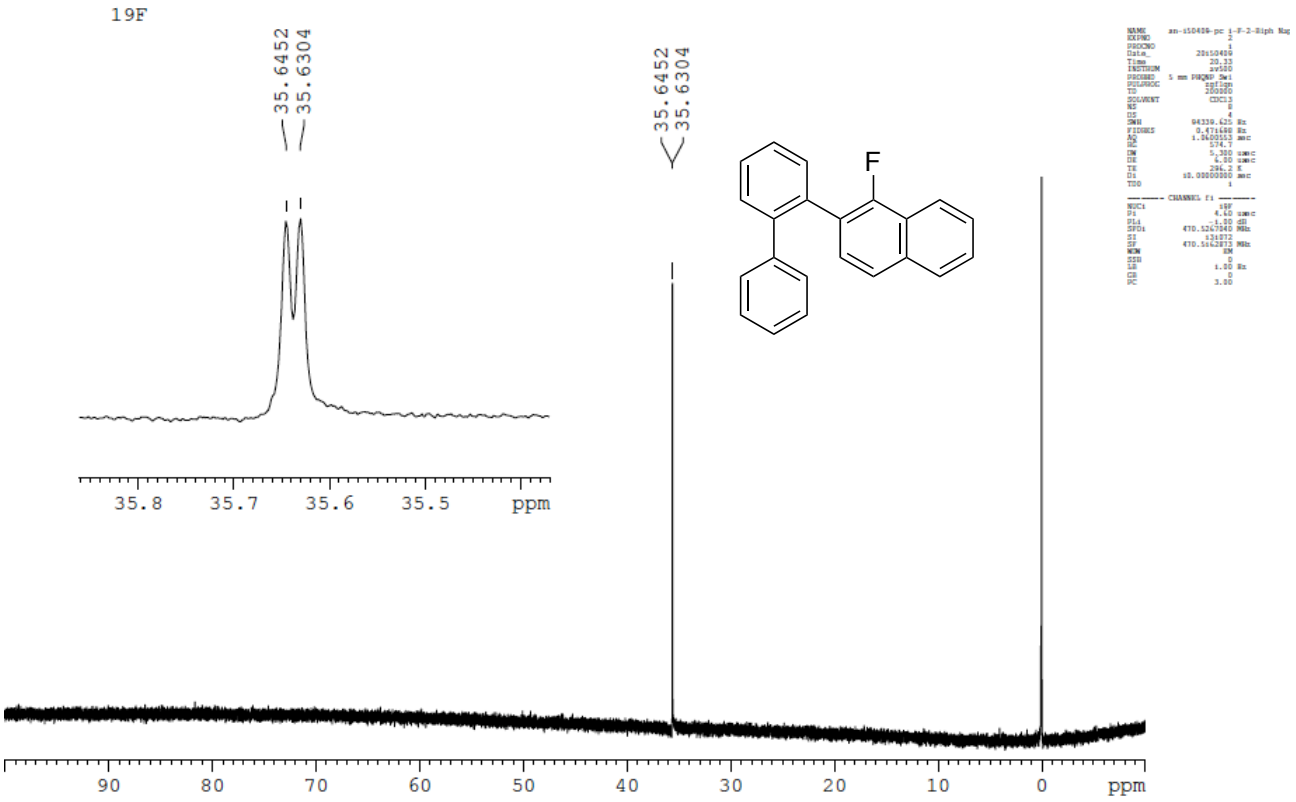
(4) S. M. Rafiq, R. Sivasakthikumaran, J. Karunakaran and A. K. Mohanakrishnan, *Eur. J. Org. Chem.*, 2015, 5099–5114.

8. ^{1}H, ^{13}C and ^{19}F NMR charts

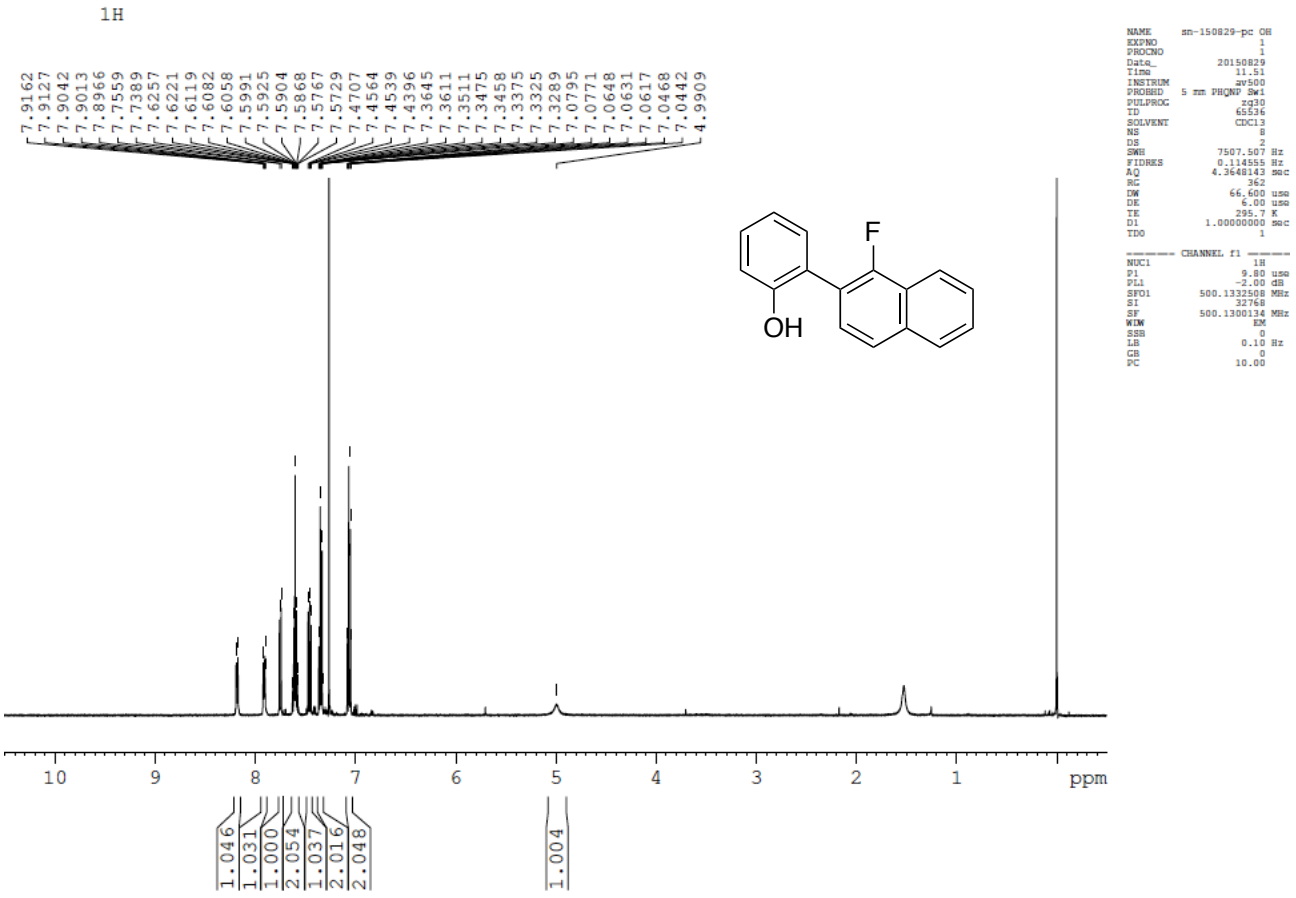
2-(Biphenyl-2-yl)-1-fluoronaphthalene (1a)

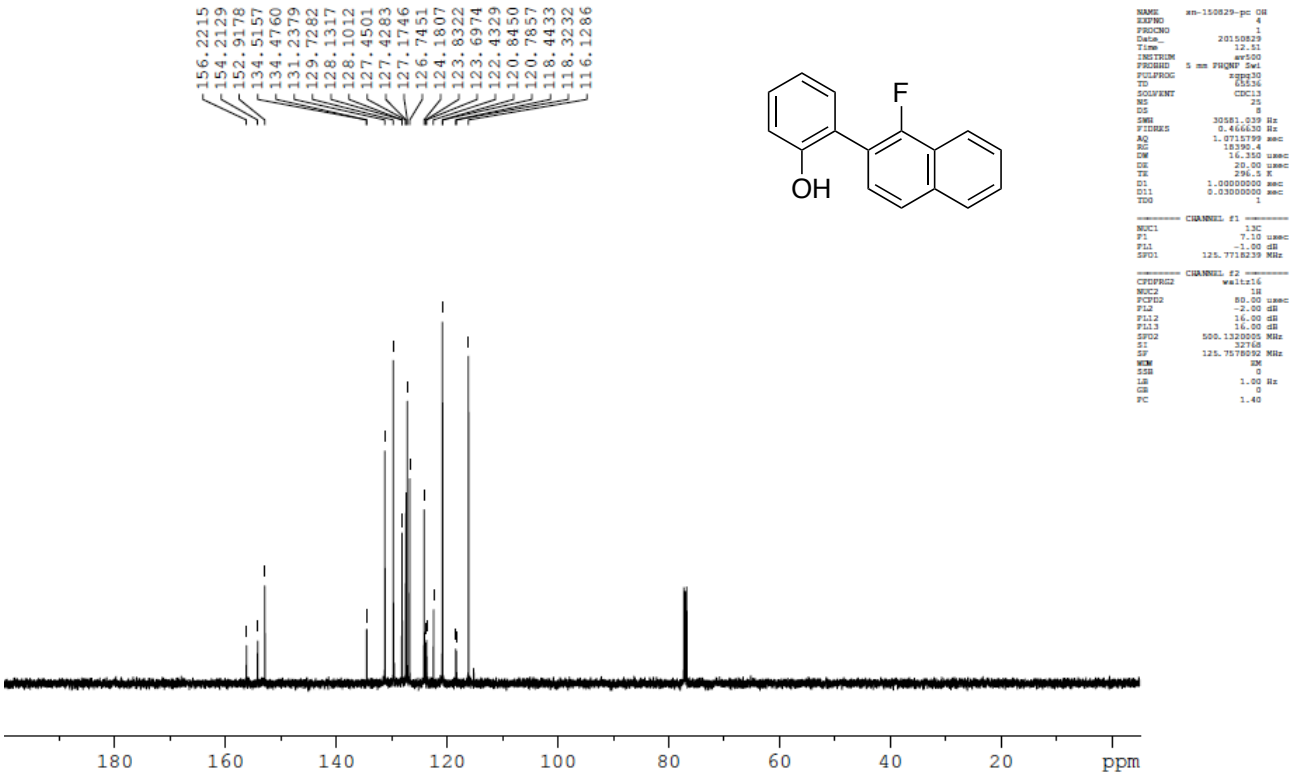






2-(1-Fluoronaphthalen-2-yl)phenol

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FIDRES 0.466630 Hz
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DE 20.00 usec
TE 296.5 K
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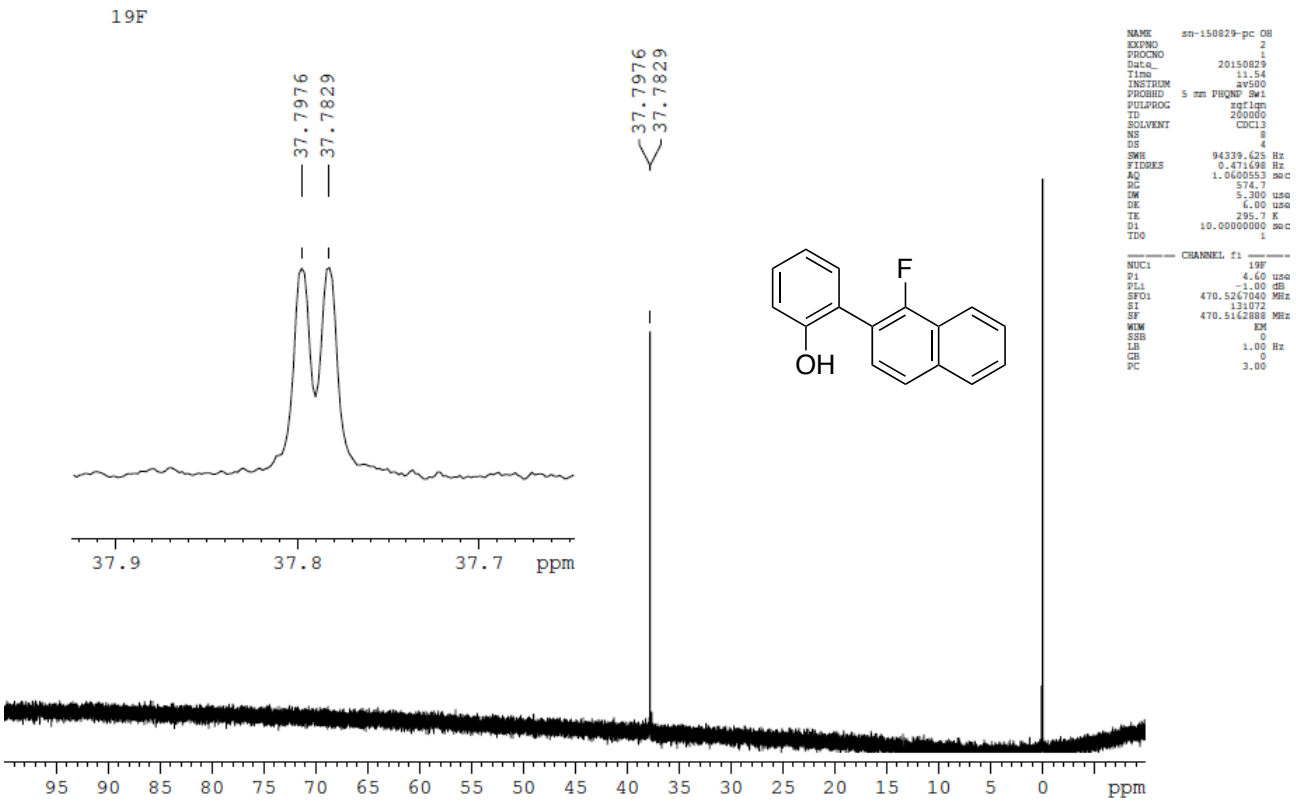
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TD 200000
SOLVENT CDCl3
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FIDRES 0.471698 Hz
AQ 1.0600553 sec
RG 574.7
DW 5.300 usec
DE 6.00 usec
TE 295.7 K
D1 10.00000000 sec
TD0 1
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NUC1 19F
P1 4.60 usec
PL1 -1.00 dB
SFO1 470.5267040 MHz
SI 131072
SF 470.5162888 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 3.00
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37.8
37.7
ppm
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90
85
80
75
70
65
60
55
50
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5
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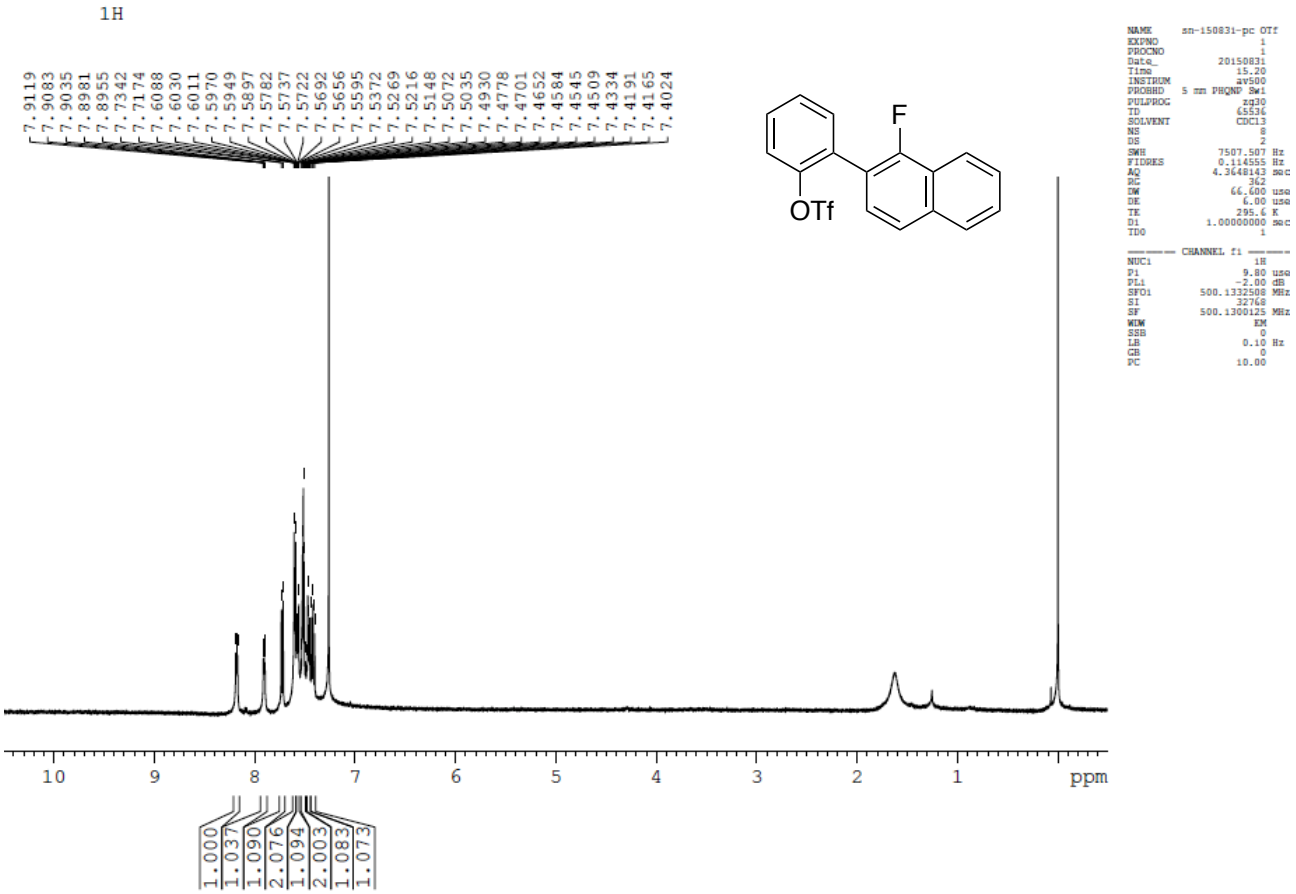
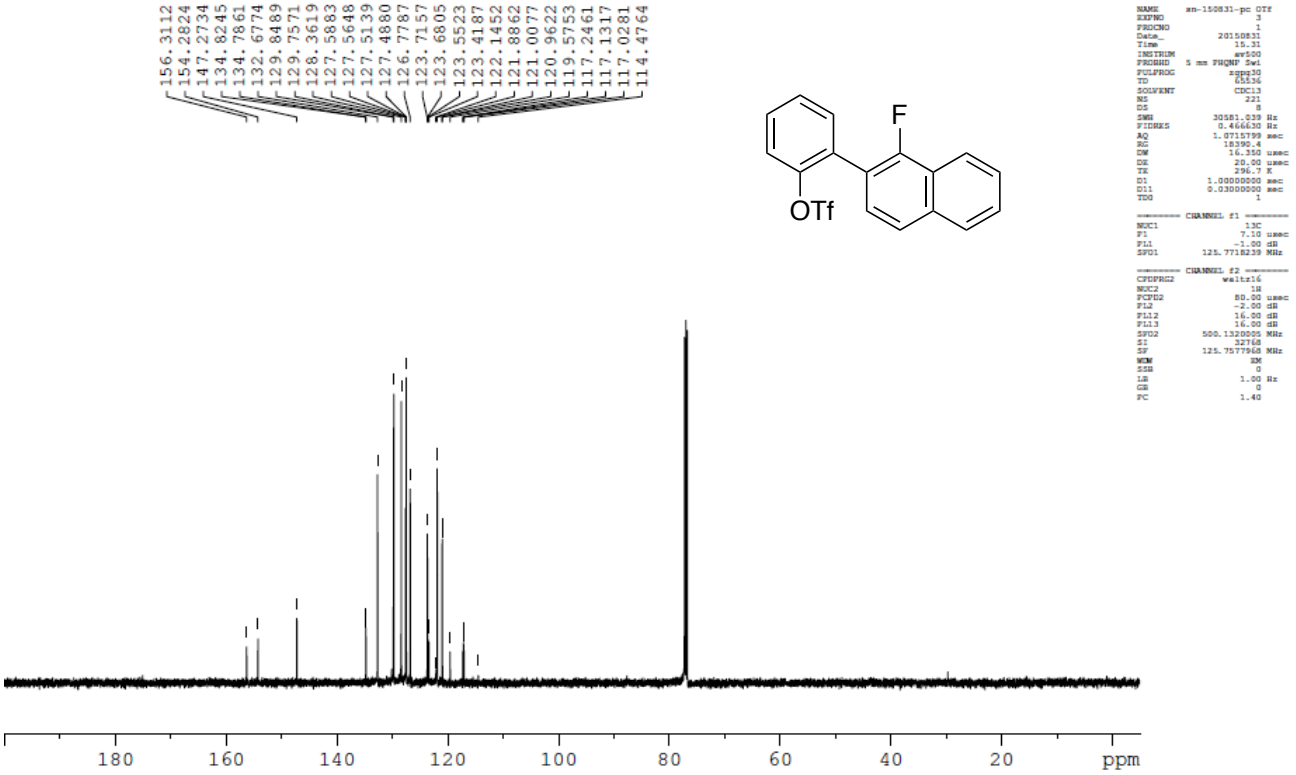
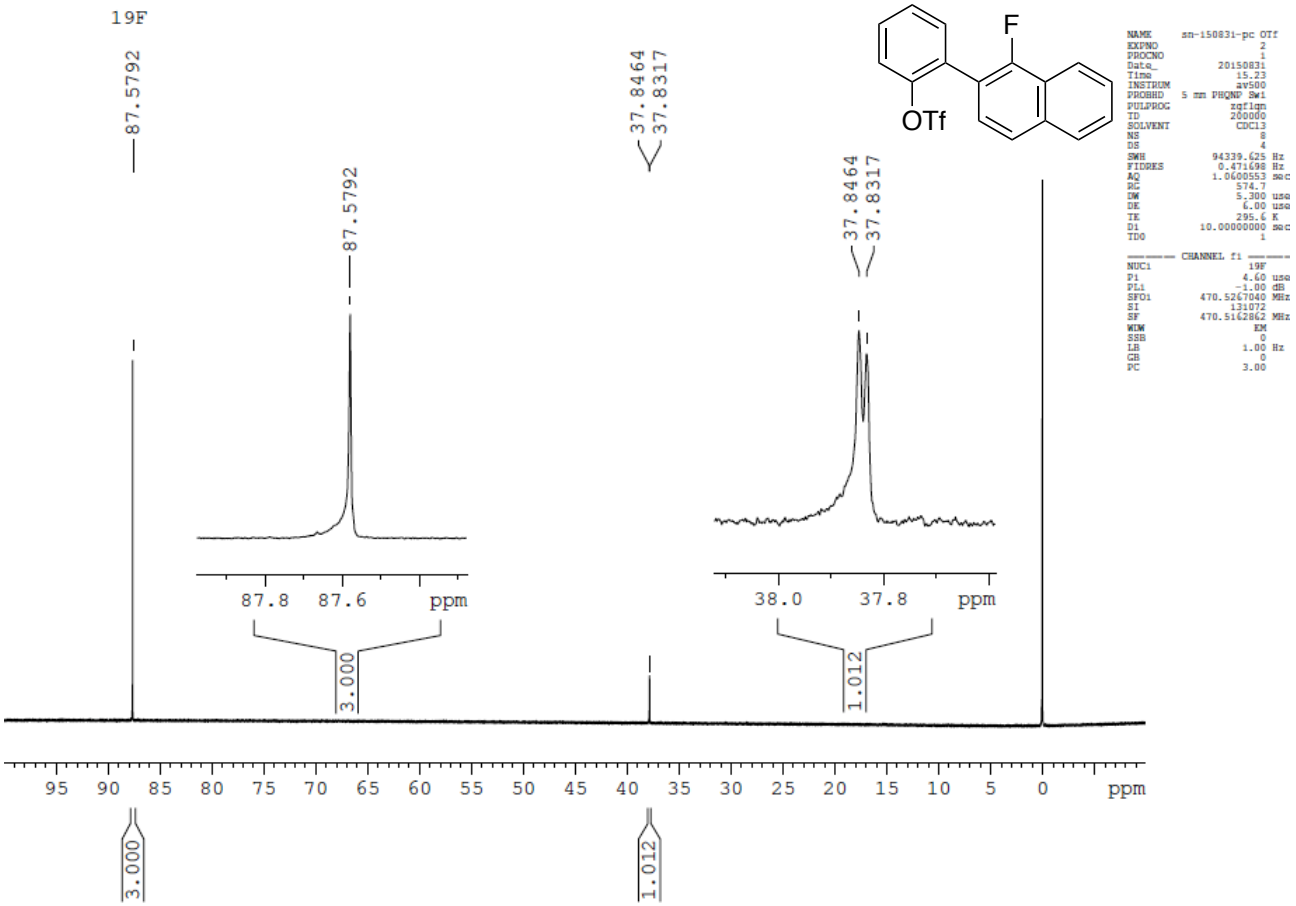
ppm

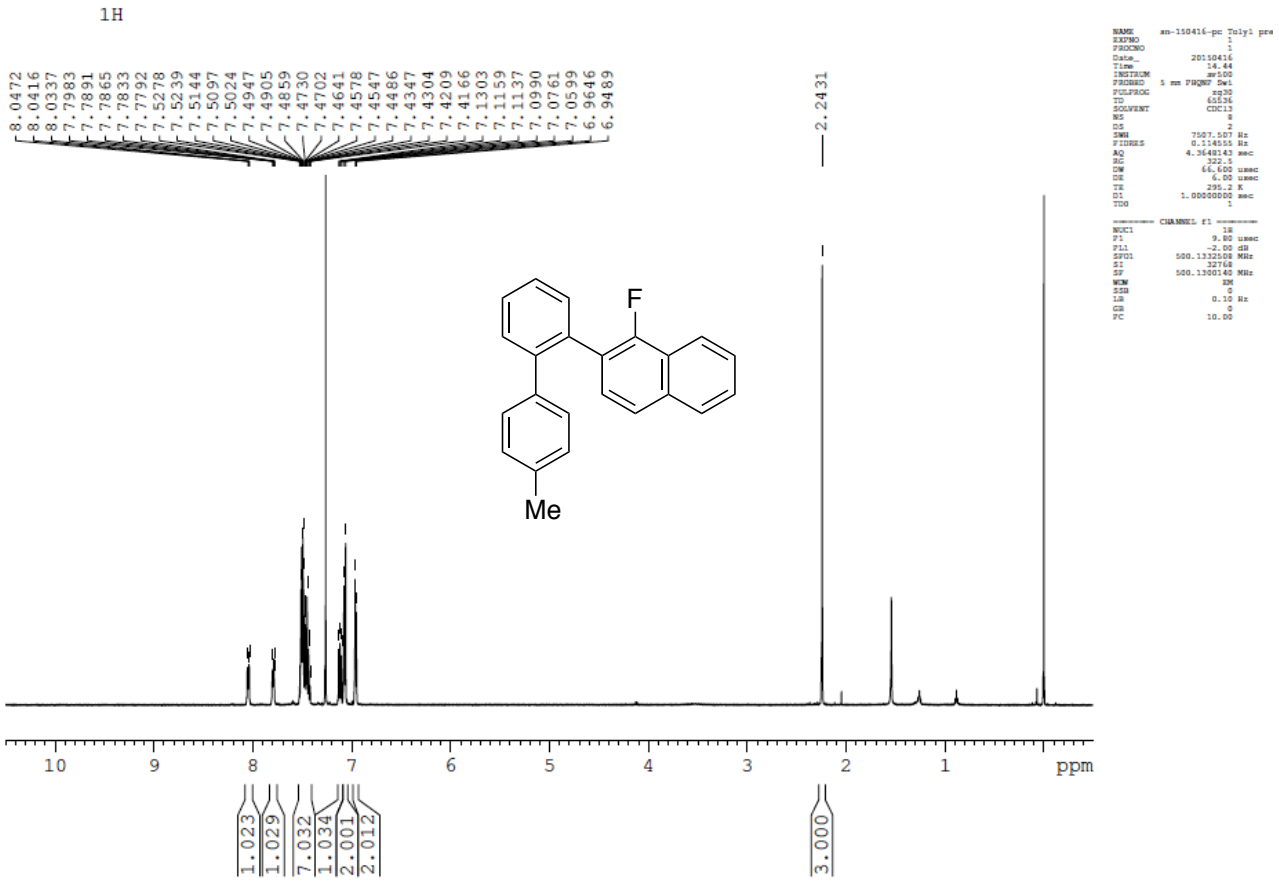
2-(1-Fluoronaphthalen-2-yl)phenyl trifluoromethanesulfonate (5)

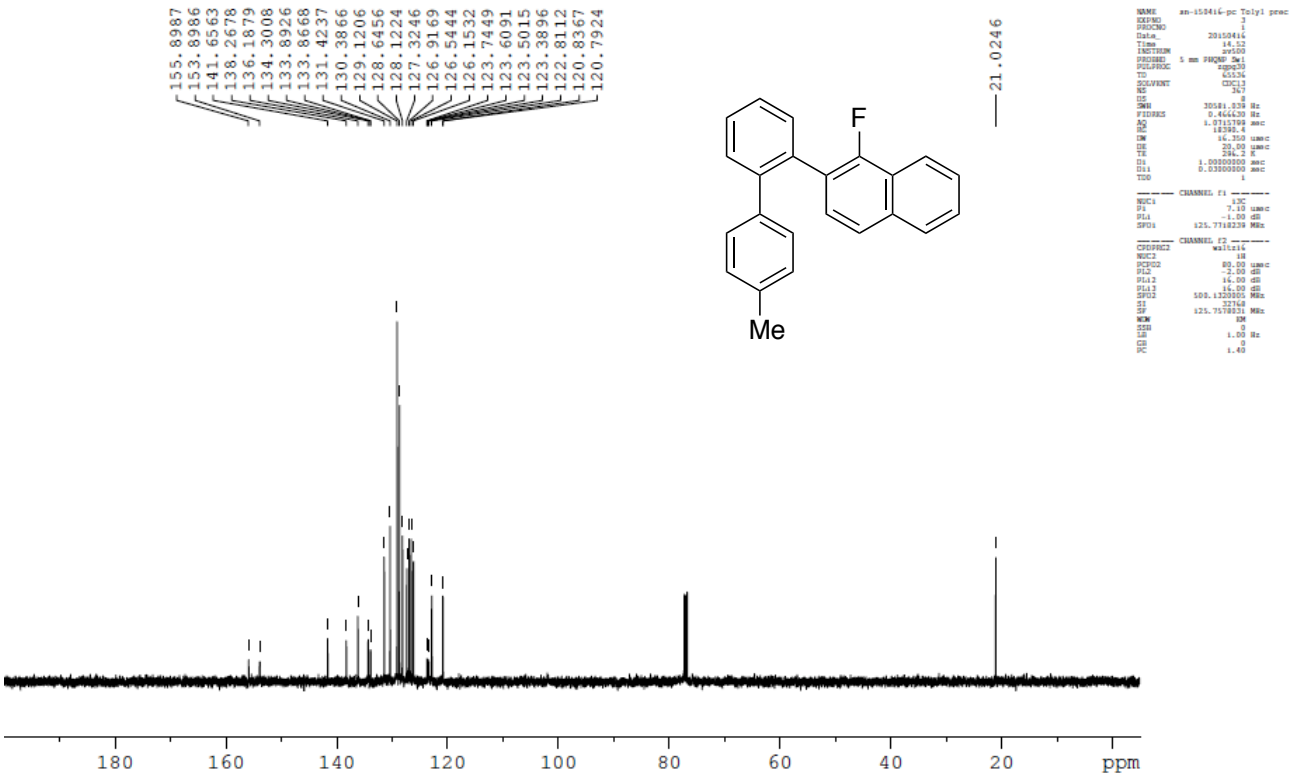






1-Fluoro-2-(4'-methylbiphenyl-2-yl)naphthalene (1b)

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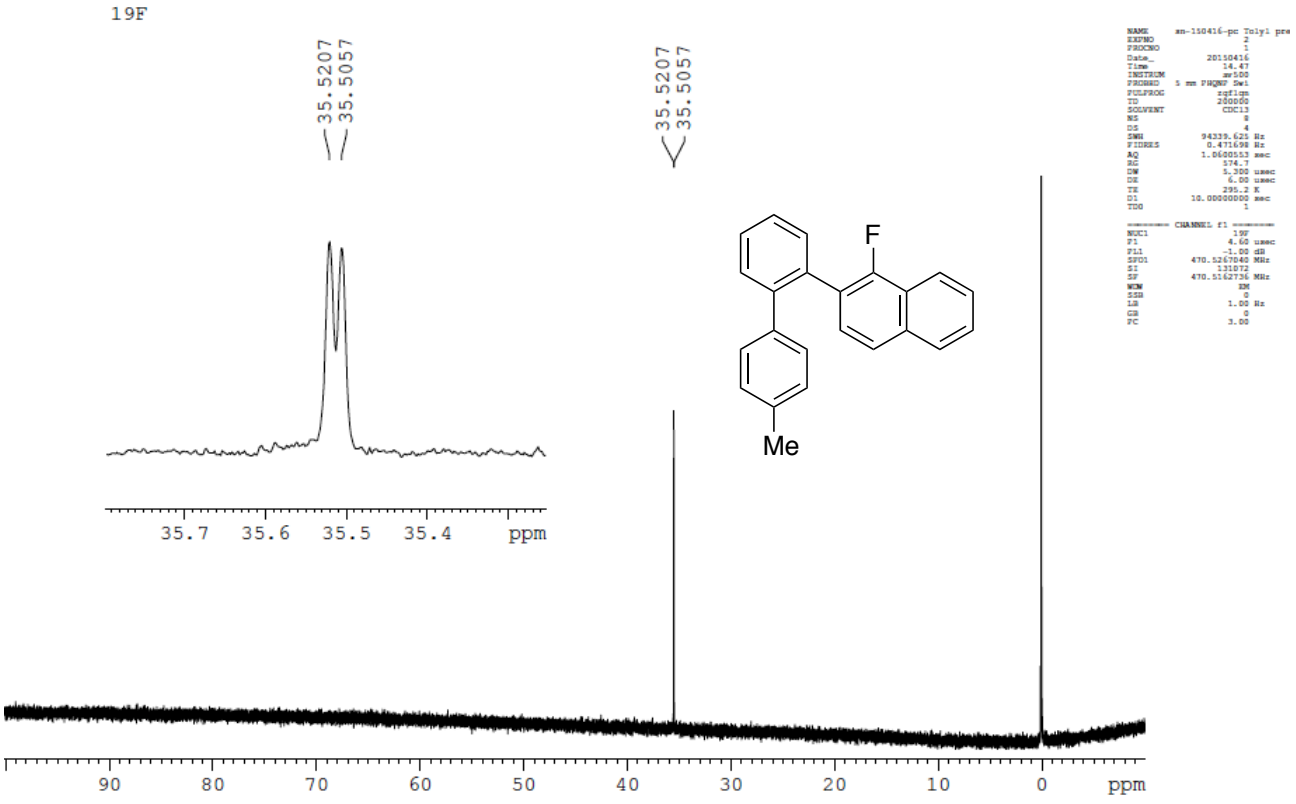
141.6563
138.2678
136.1879
134.3008
133.8926
133.8668
131.4237
130.3866
129.1206
128.6456
128.1224
127.3246
126.9169
126.5444
126.1532
123.7449
123.6091
123.5015
123.3896
122.8112
120.8367
120.7924
21.0246
F
Me
180
160
140
120
100
80
60
40
20
ppm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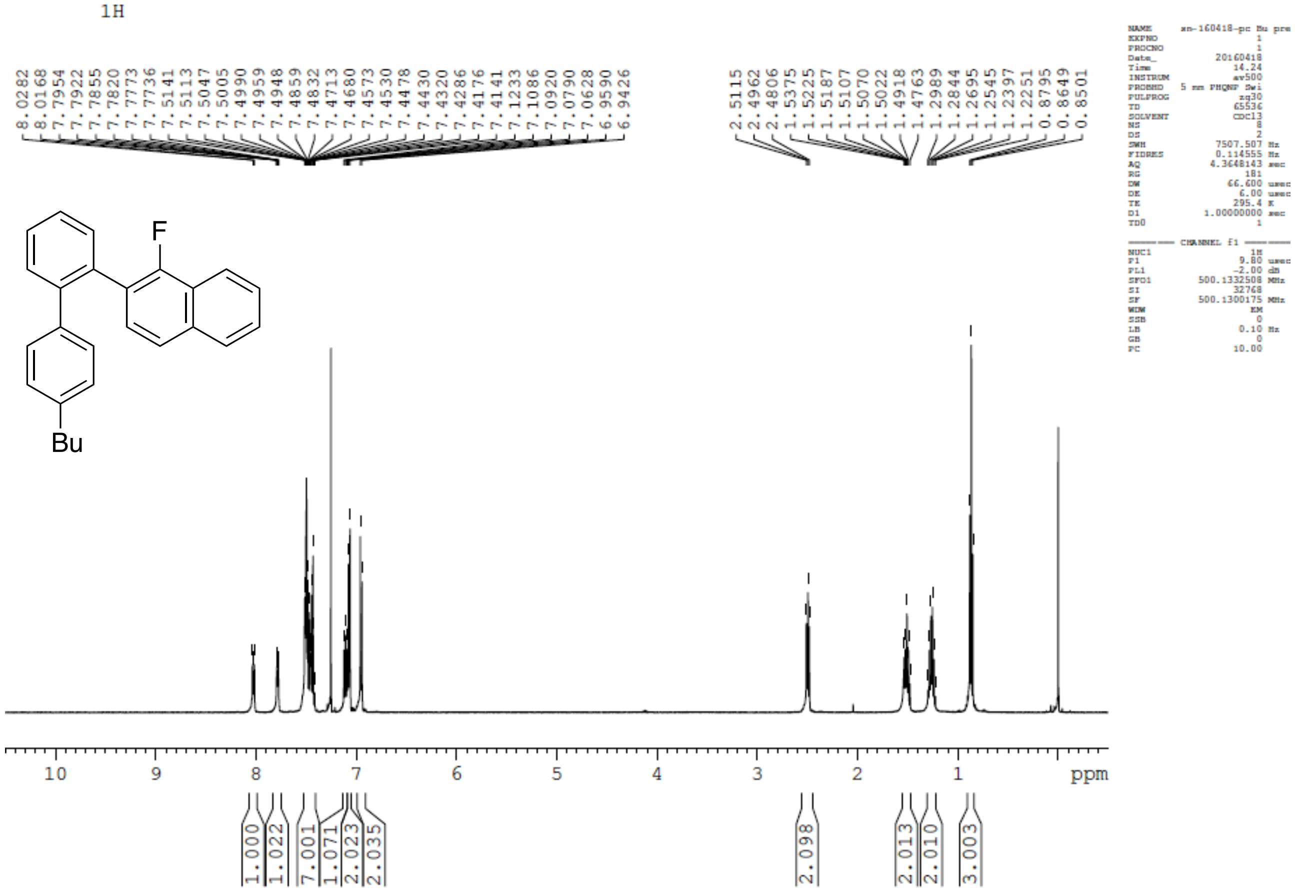
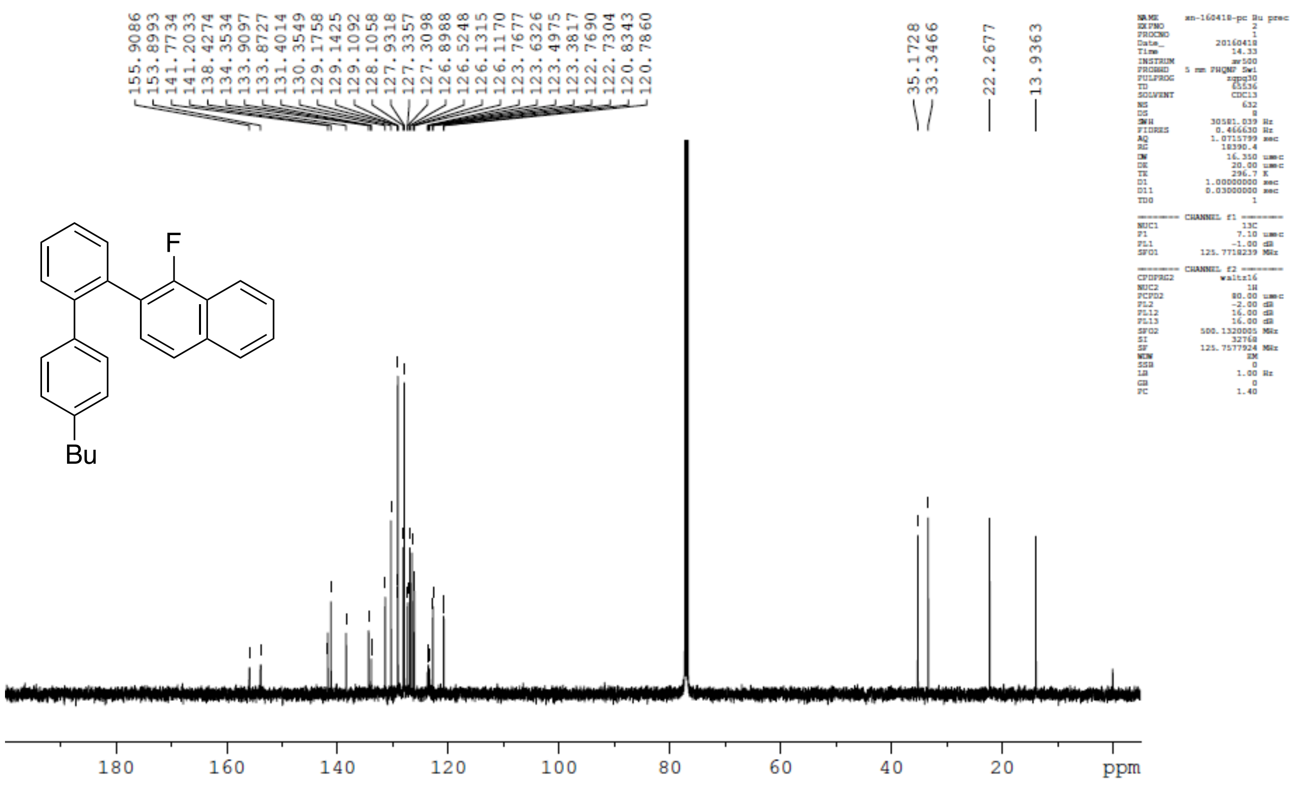
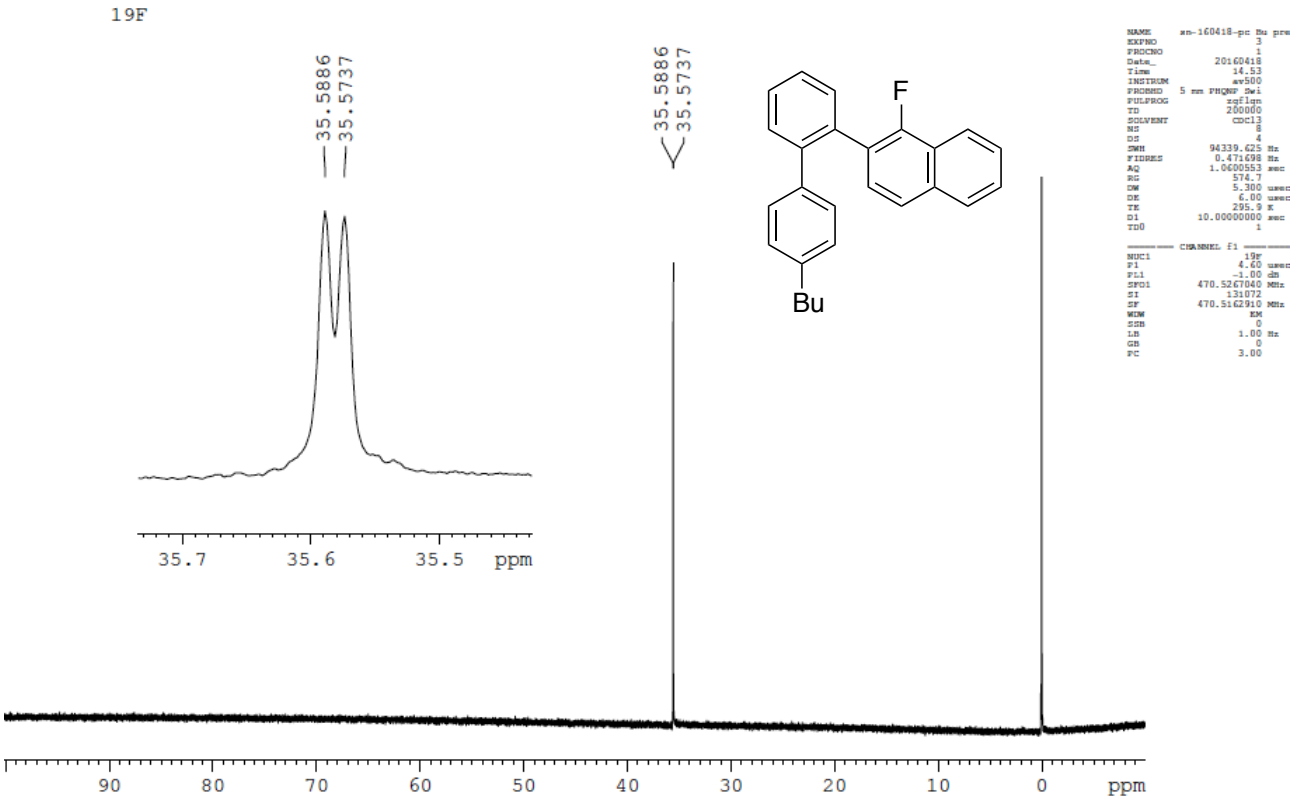
35.5207
35.5057
F
Me
35.7
35.6
35.5
35.4
ppm
90
80
70
60
50
40
30
20
10
0
ppm

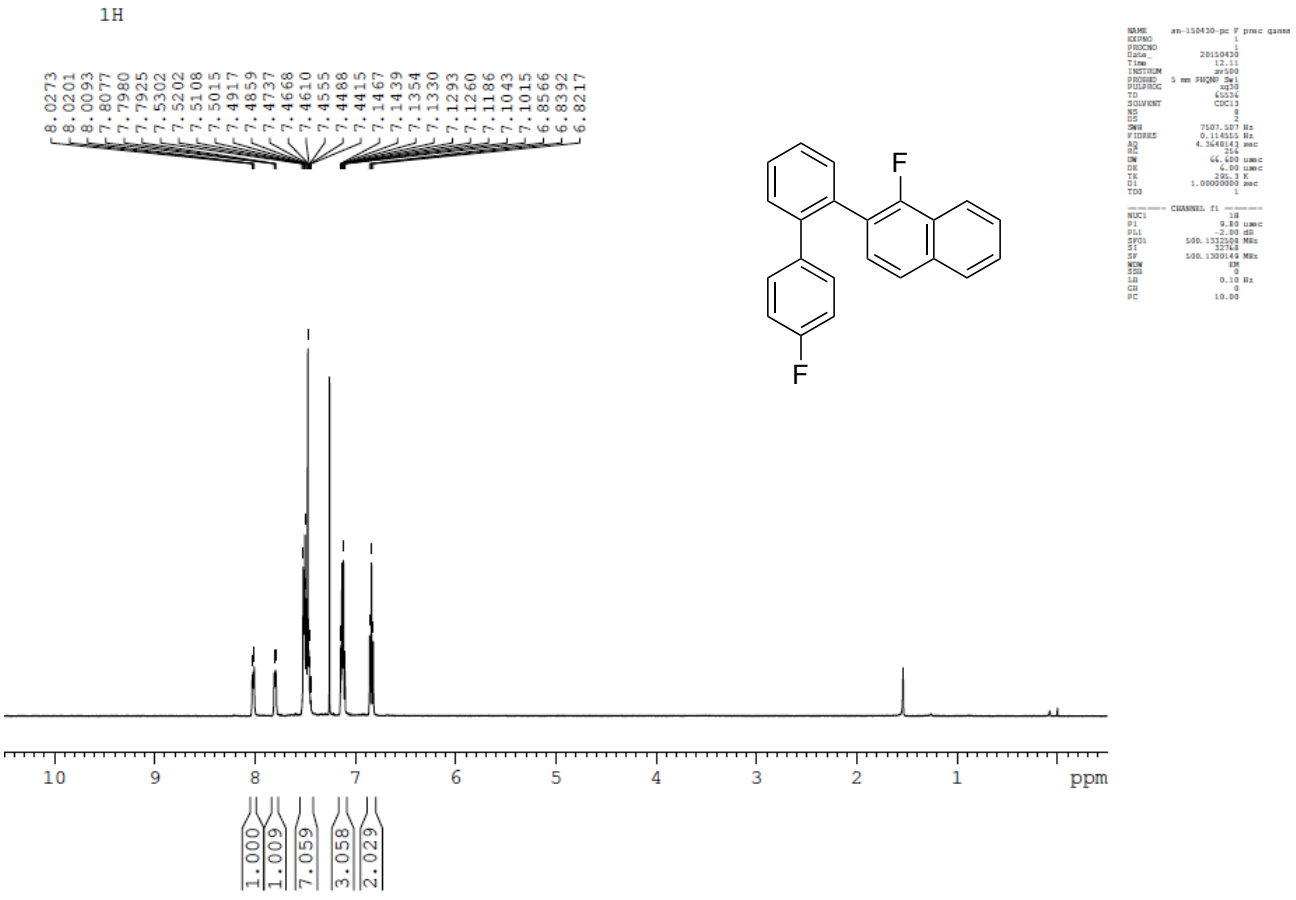
2-(4'-Butylbiphenyl-2-yl)-1-fluoronaphthalene (1c)

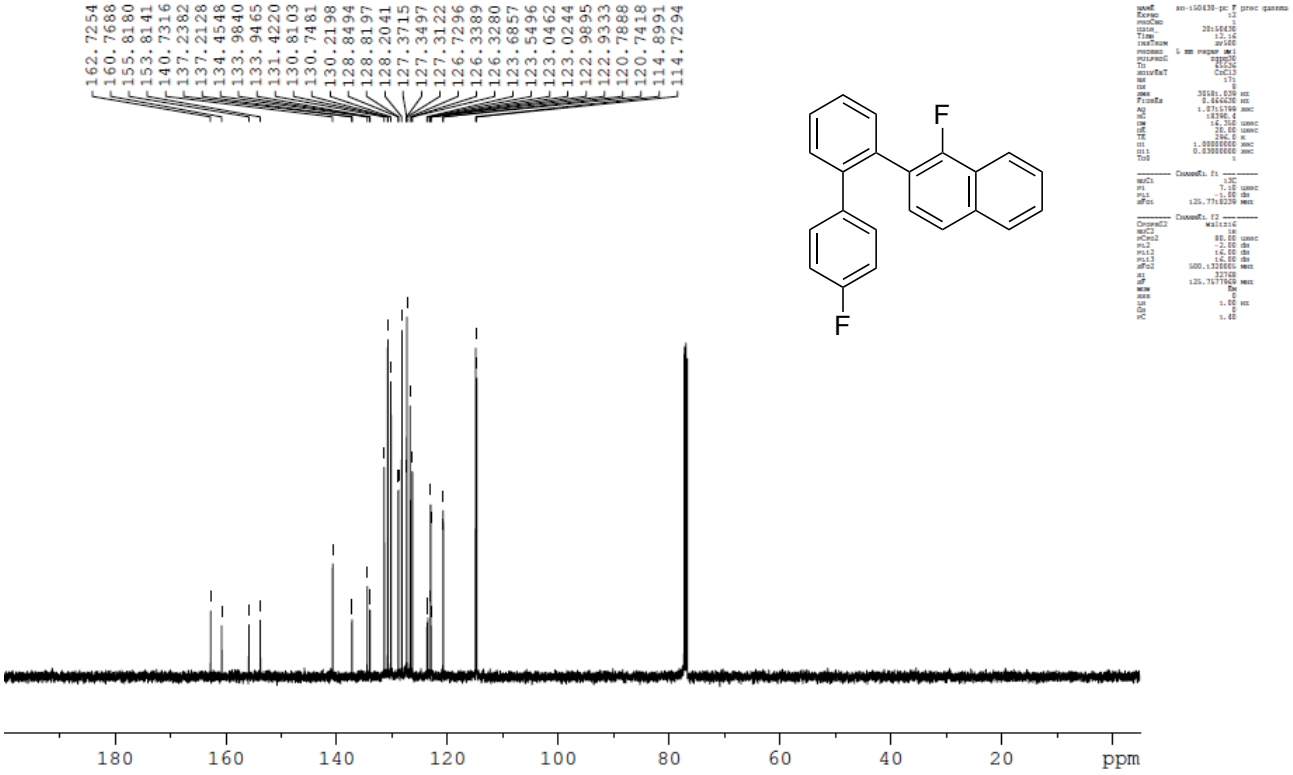






1-Fluoro-2-(4'-fluorobiphenyl-2-yl)naphthalene (1d)

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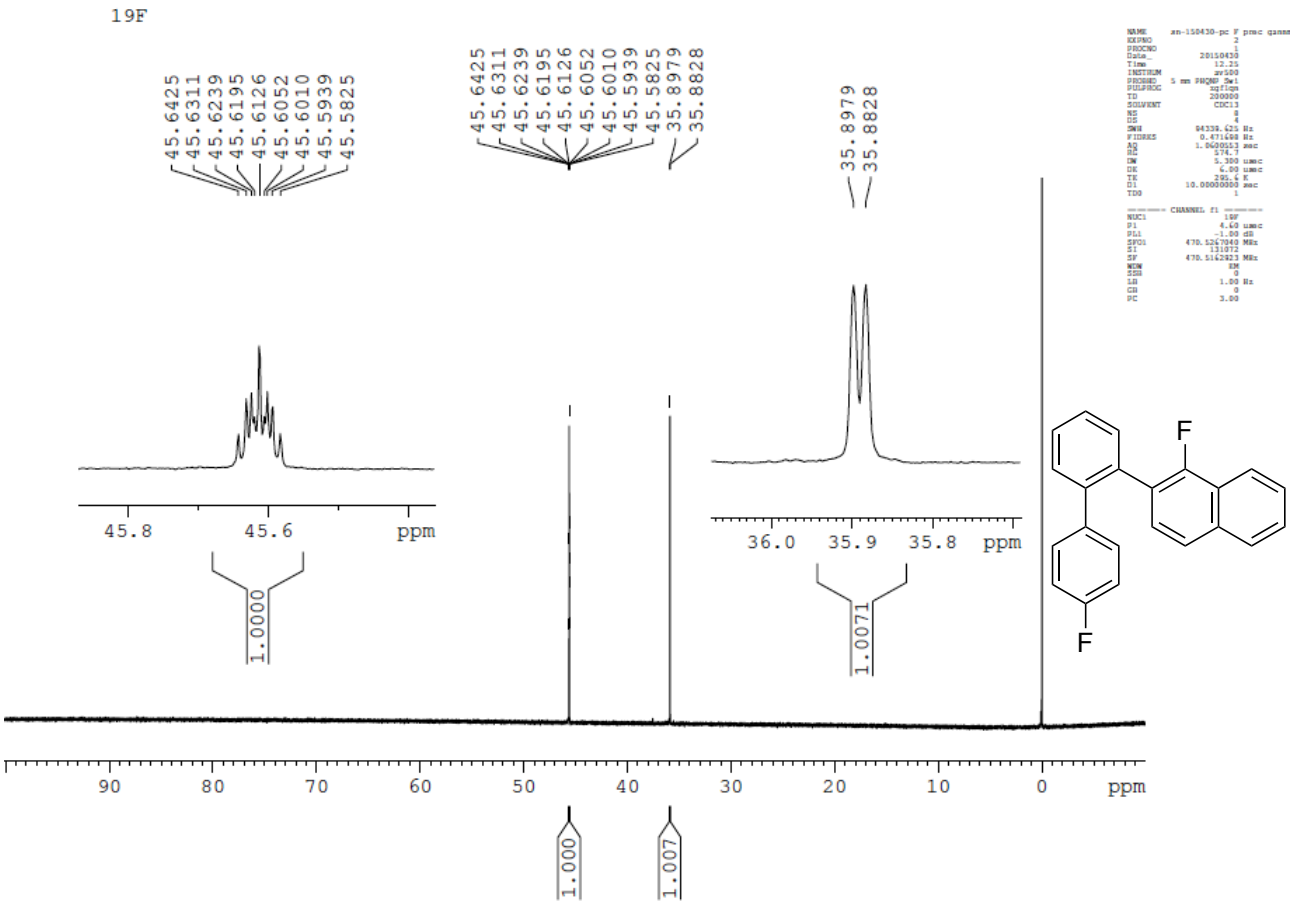
160.7688
155.8180
153.8141
140.7316
137.2382
137.2128
134.4548
133.9840
133.9465
131.4220
130.8103
130.7481
130.2198
128.8494
128.8197
128.2041
127.3715
127.3497
127.3122
126.7296
126.3389
126.3280
123.6857
123.5496
123.0462
123.0244
122.9895
122.9333
120.7888
120.7418
114.8991
114.7294
F
F
180
160
140
120
100
80
60
40
20
ppm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45.6425
45.6311
45.6239
45.6195
45.6126
45.6052
45.6010
45.5939
45.5825
45.6425
45.6311
45.6239
45.6195
45.6126
45.6052
45.6010
45.5939
45.5825
35.8979
35.8828
35.8979
35.8828
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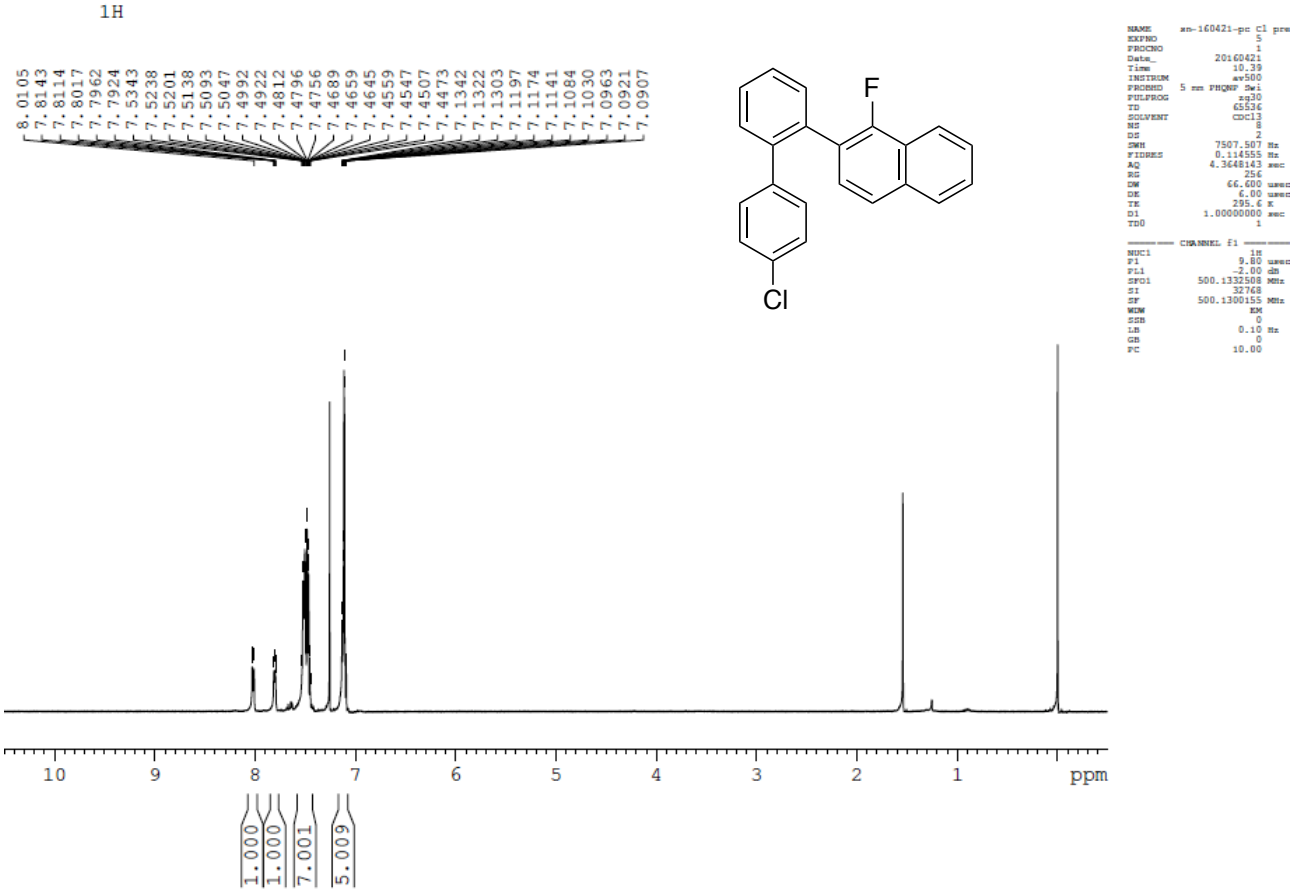
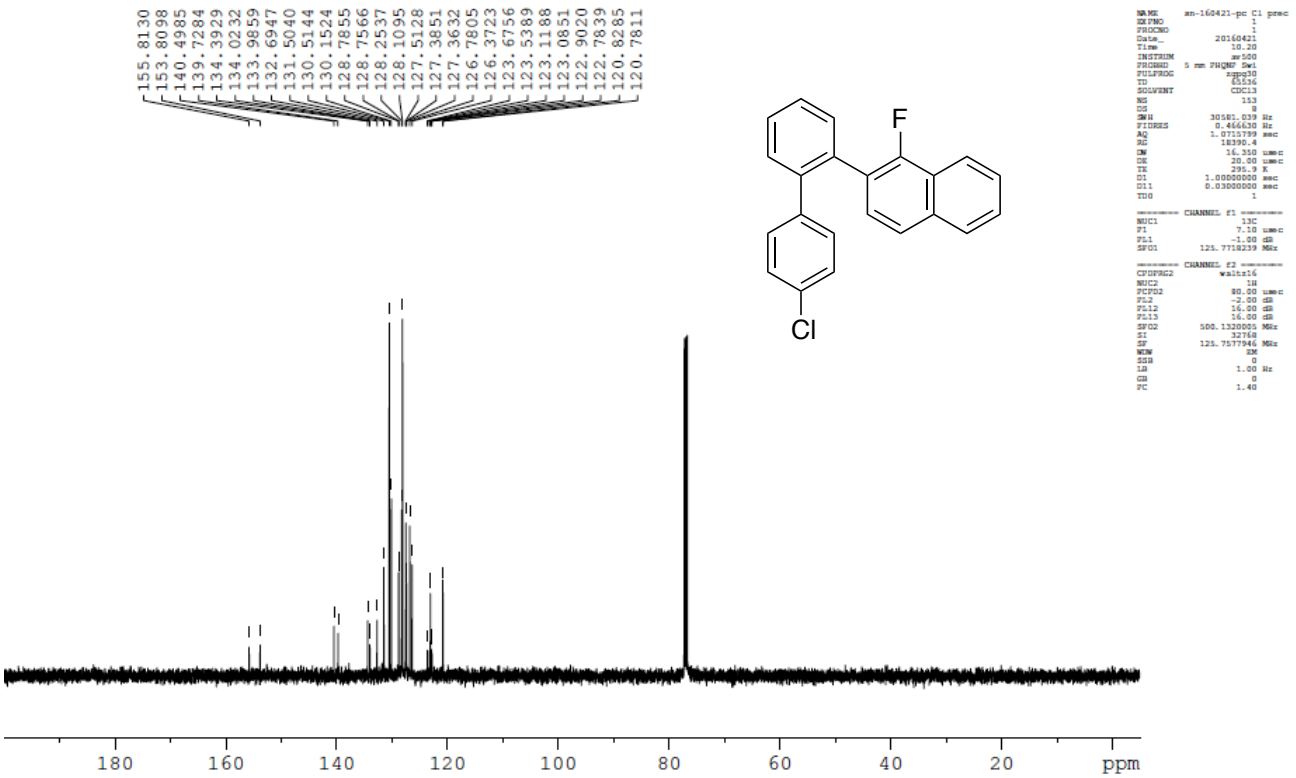
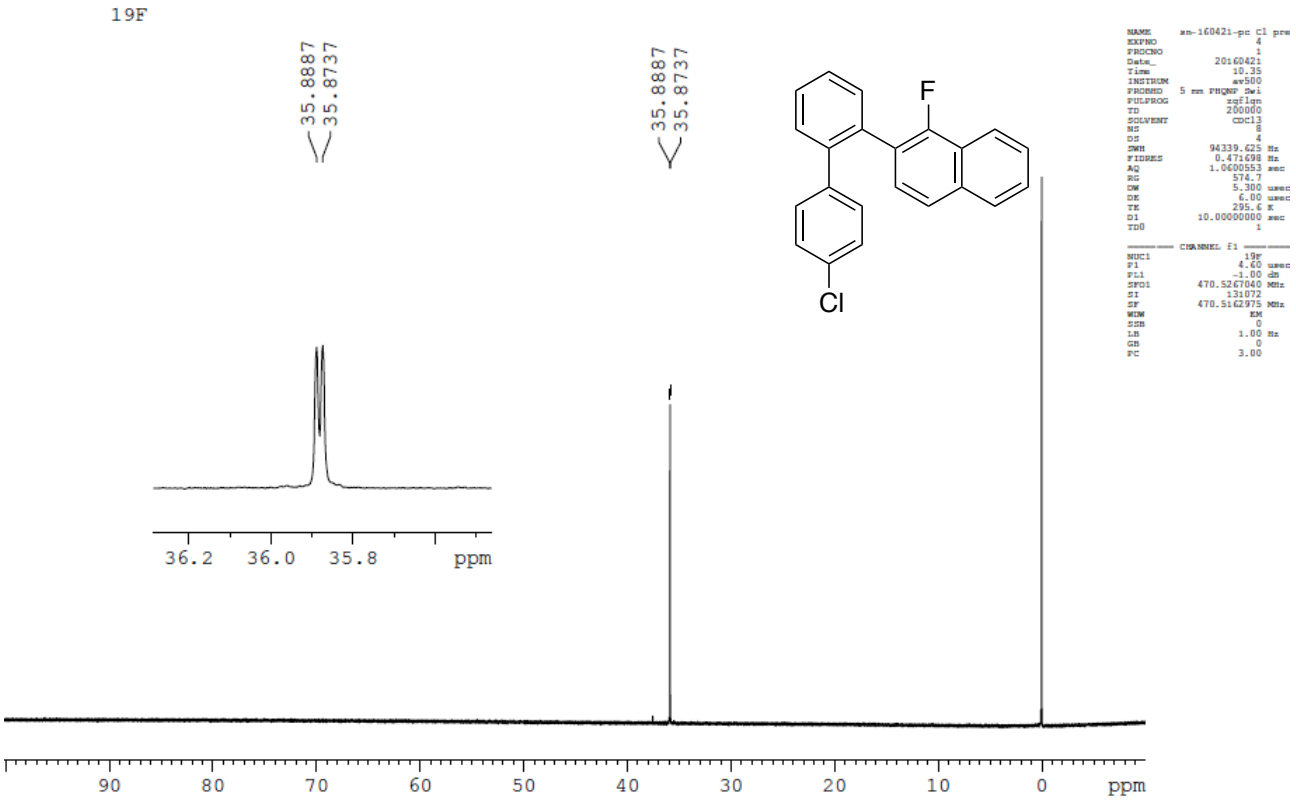
45.6
ppm
1.0000
36.0
35.9
35.8
ppm
1.0071
F
F
90
80
70
60
50
40
30
20
10
0
ppm
1.000
1.007

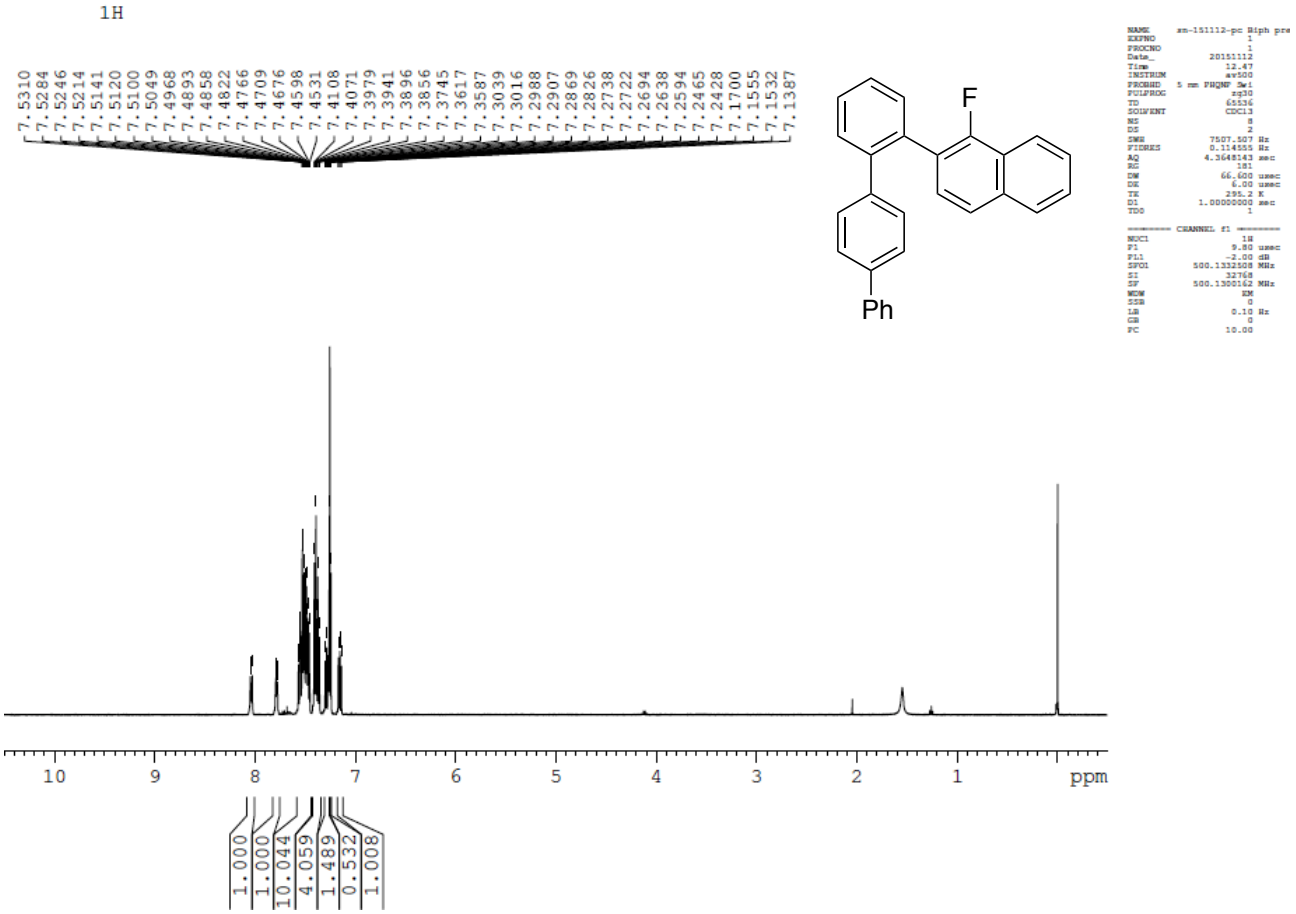
2-(4'-Chlorobiphenyl-2-yl)-1-fluoronaphthalene (1e)

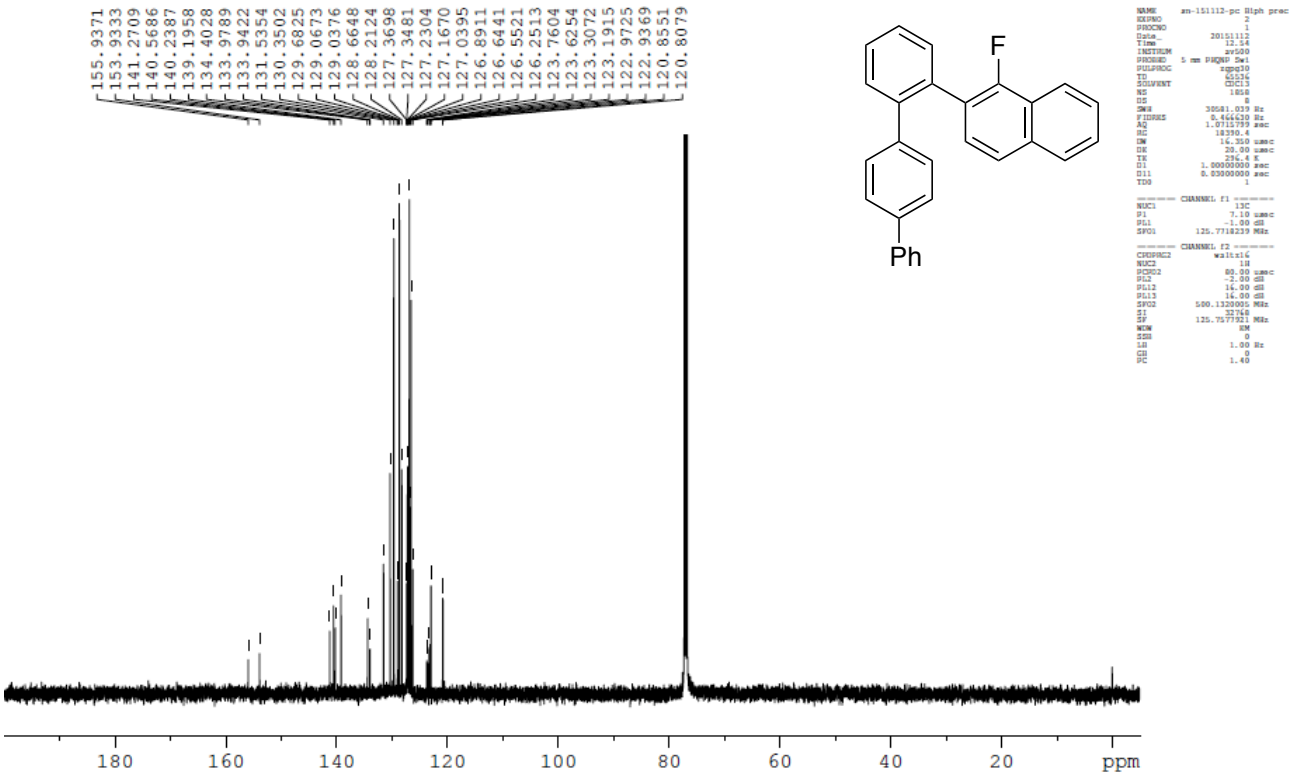






1-Fluoro-2-(1,1':4',1''-terphenyl-2-yl)naphthalene (1f)

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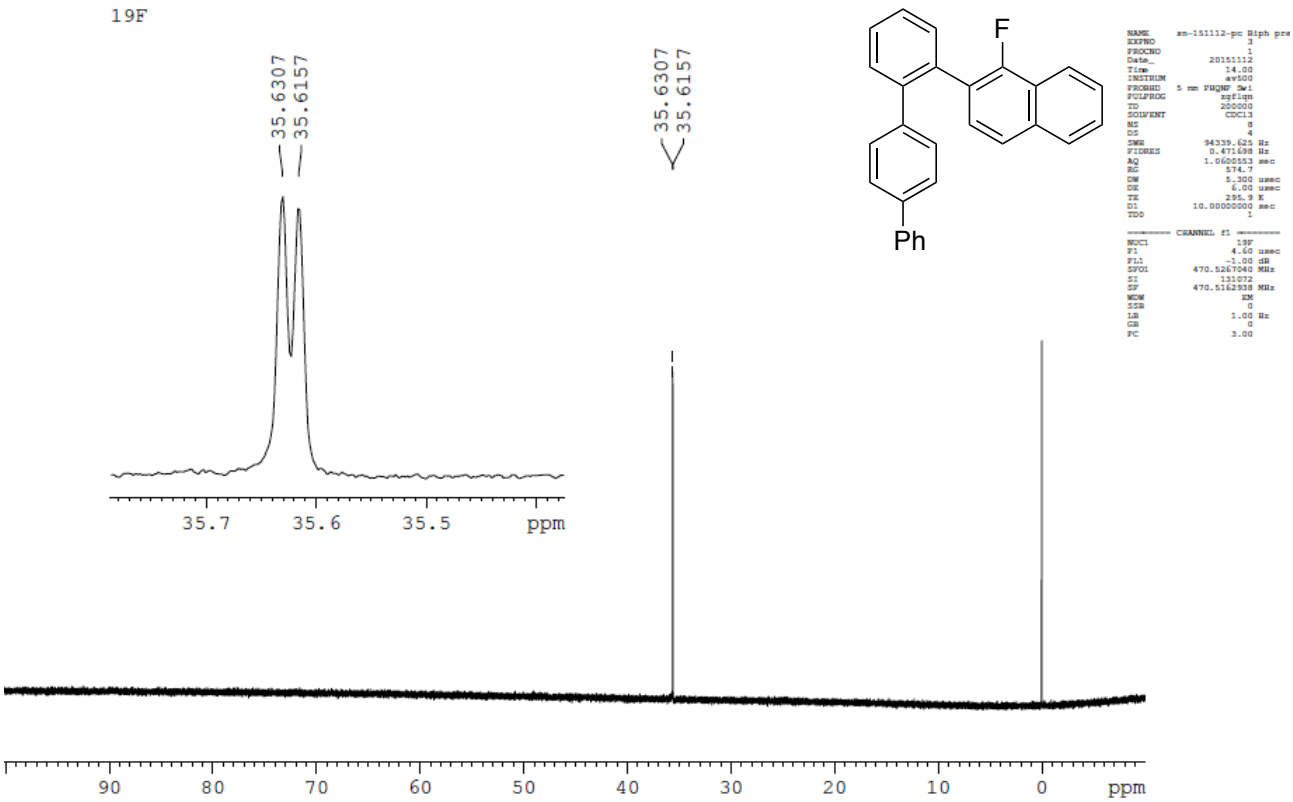
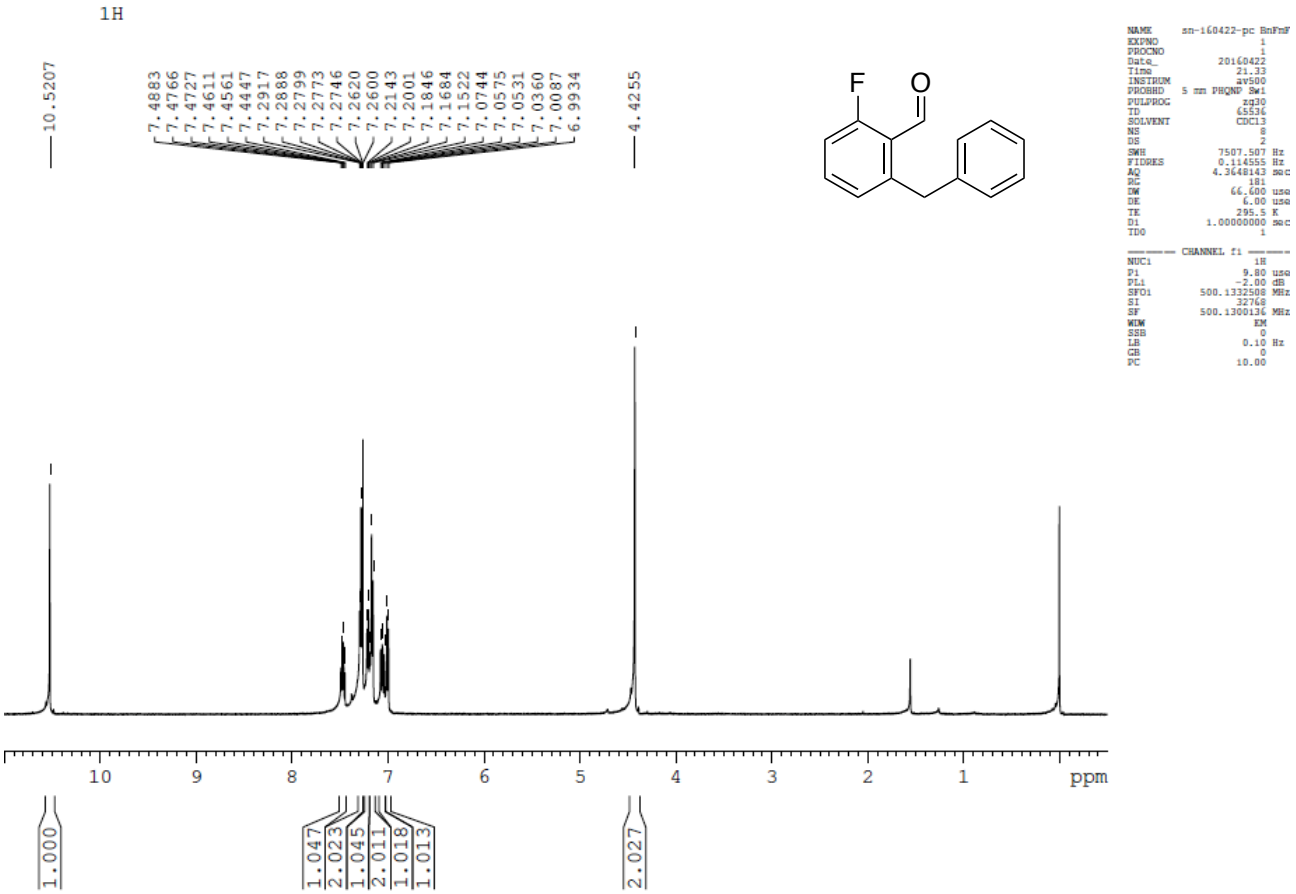
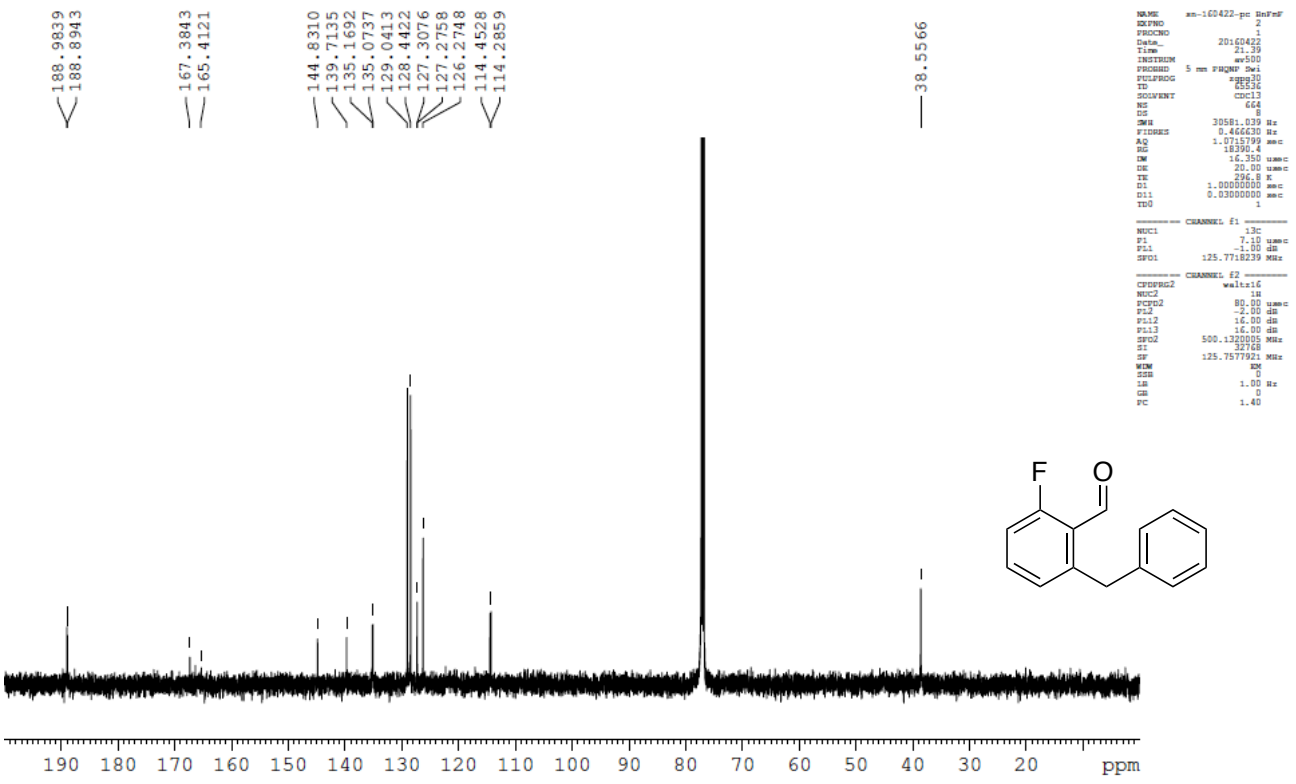
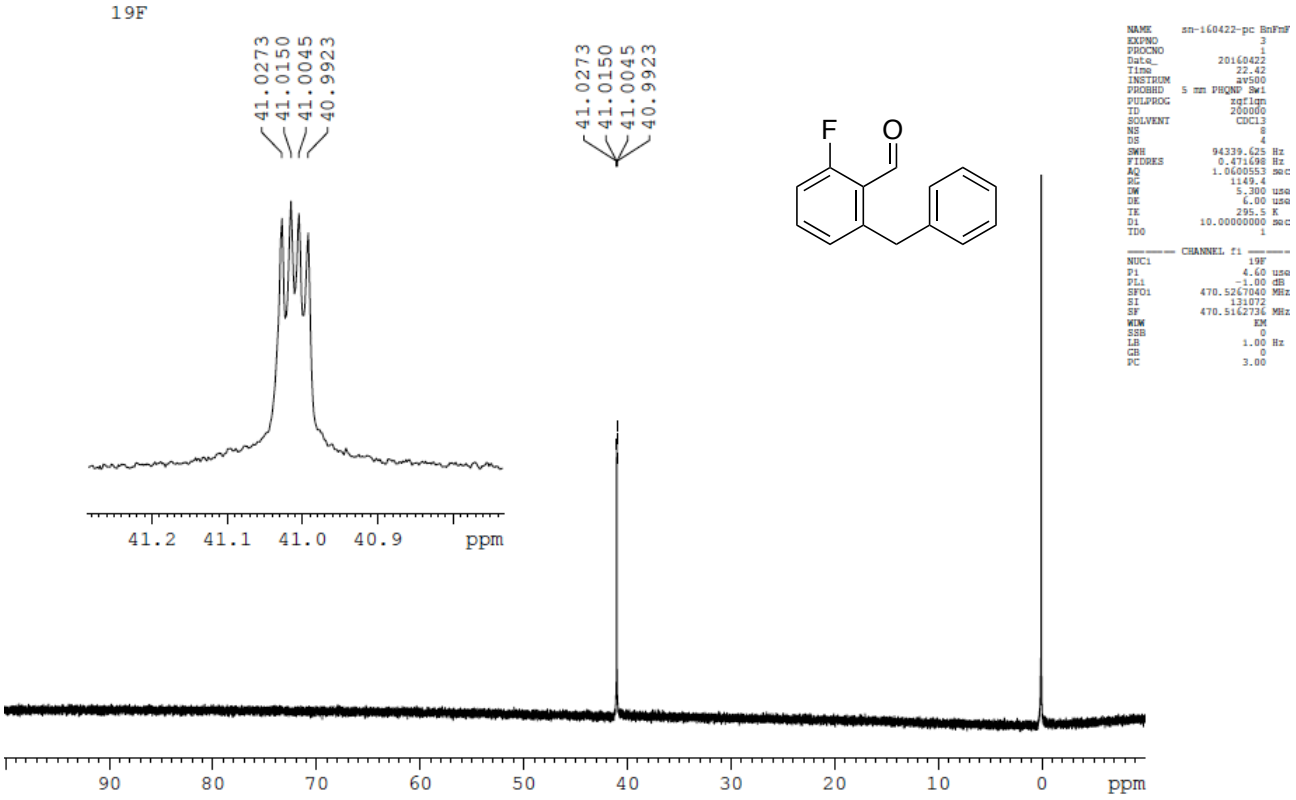
153.9333
141.2709
140.5686
140.2387
139.1958
134.4028
133.9789
133.9422
131.5354
130.3502
129.6825
129.0673
129.0376
128.6648
128.2124
127.3698
127.3481
127.2304
127.1670
127.0395
126.8911
126.6441
126.5521
126.2513
123.7604
123.6254
123.3072
123.1915
122.9725
122.9369
120.8551
120.8079
F
Ph
180
160
140
120
100
80
60
40
20
ppm


19F
35.6307
35.6157
35.6307
35.6157
F
Ph
35.7
35.6
35.5
ppm
90
80
70
60
50
40
30
20
10
0
ppm

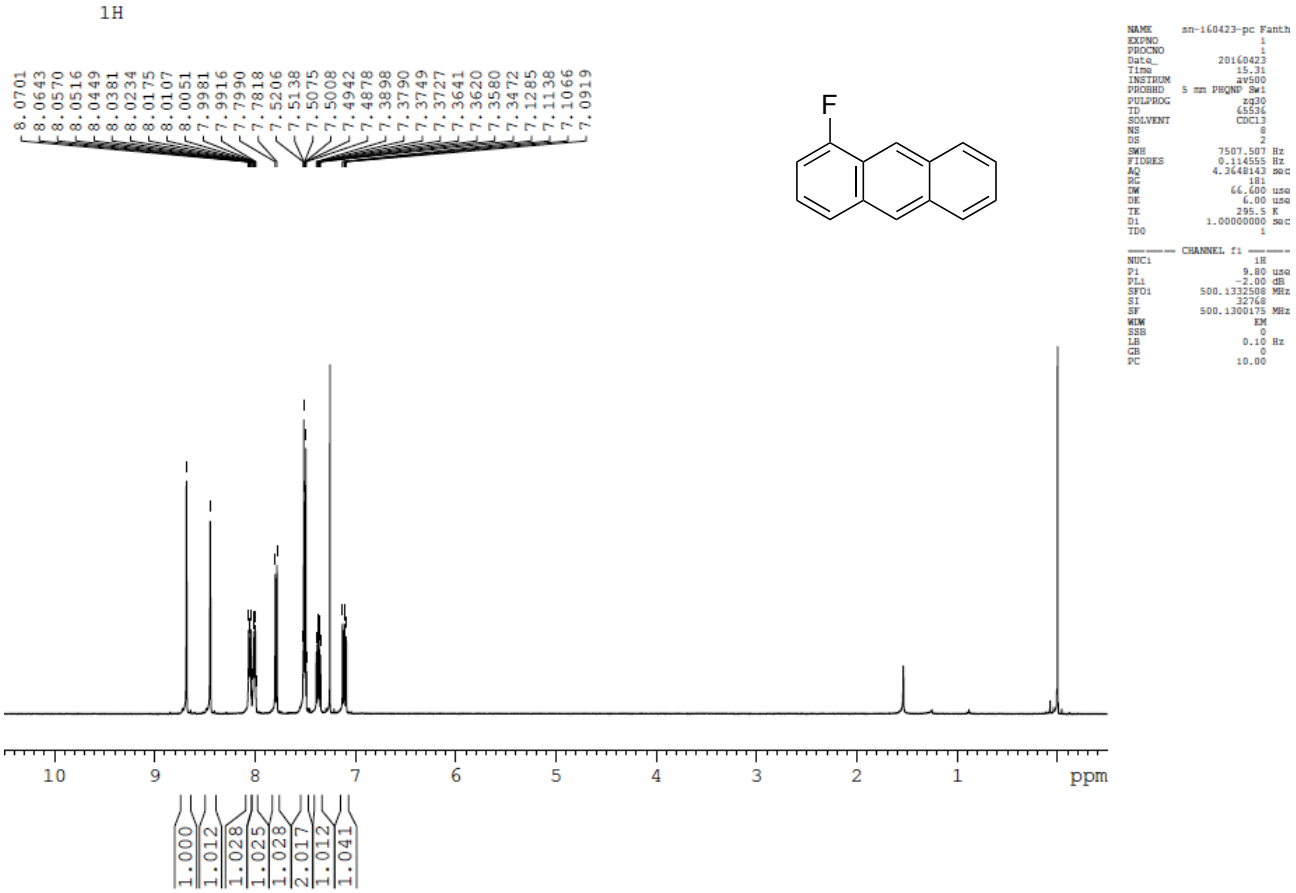
2-Benzyl-6-fluorobenzaldehyde

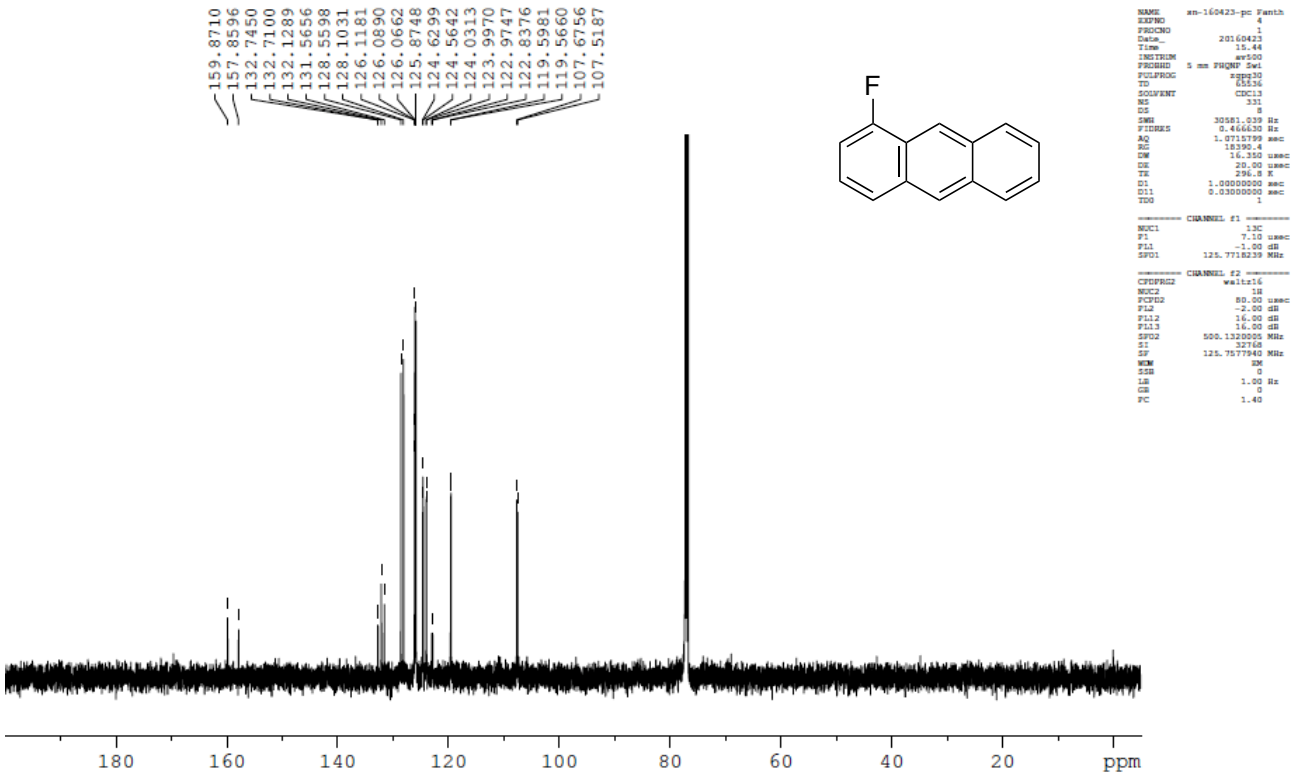






1-Fluoroanthracene

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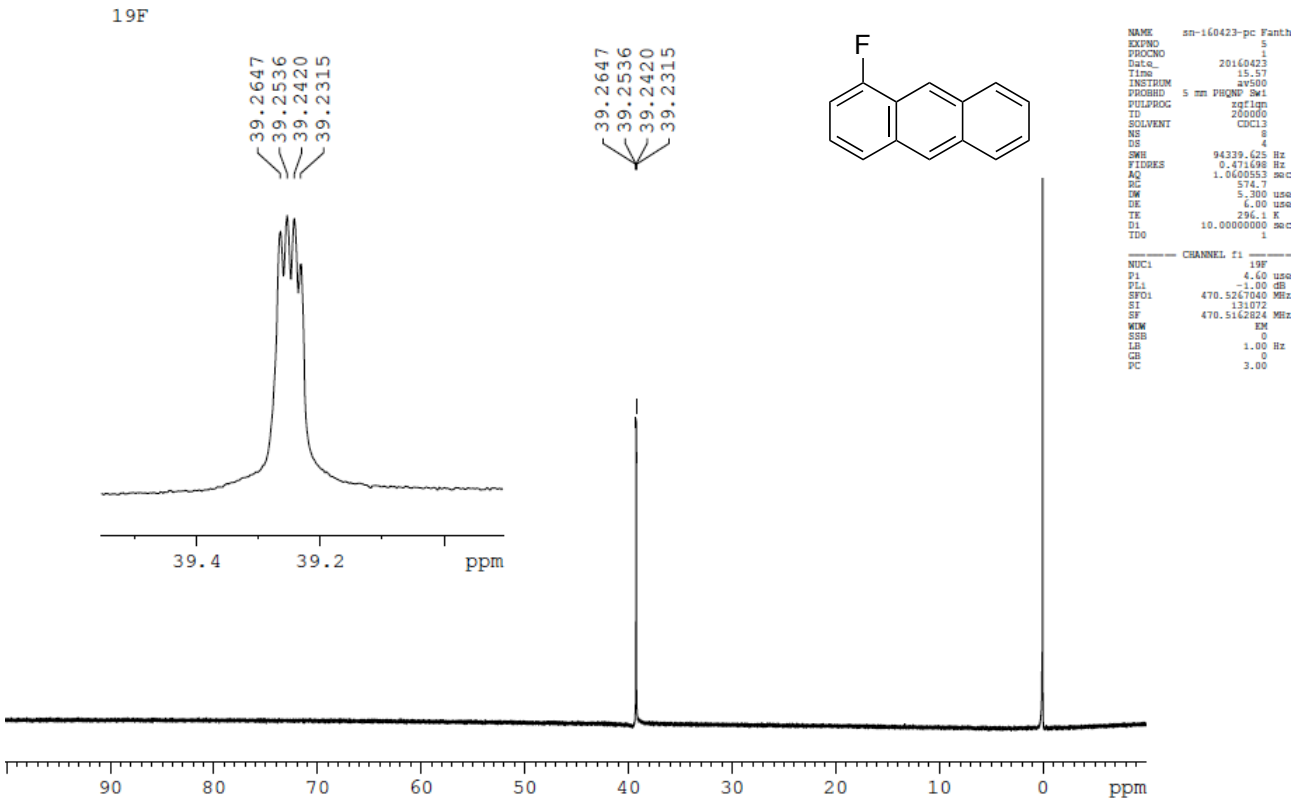
157.8596
132.7450
132.7100
132.1289
131.5656
128.5598
128.1031
126.1181
126.0890
126.0662
125.8748
124.6299
124.5642
124.0313
123.9970
122.9747
122.8376
119.5981
119.5660
107.6756
107.5187
F
180
160
140
120
100
80
60
40
20
ppm


19F
39.2647
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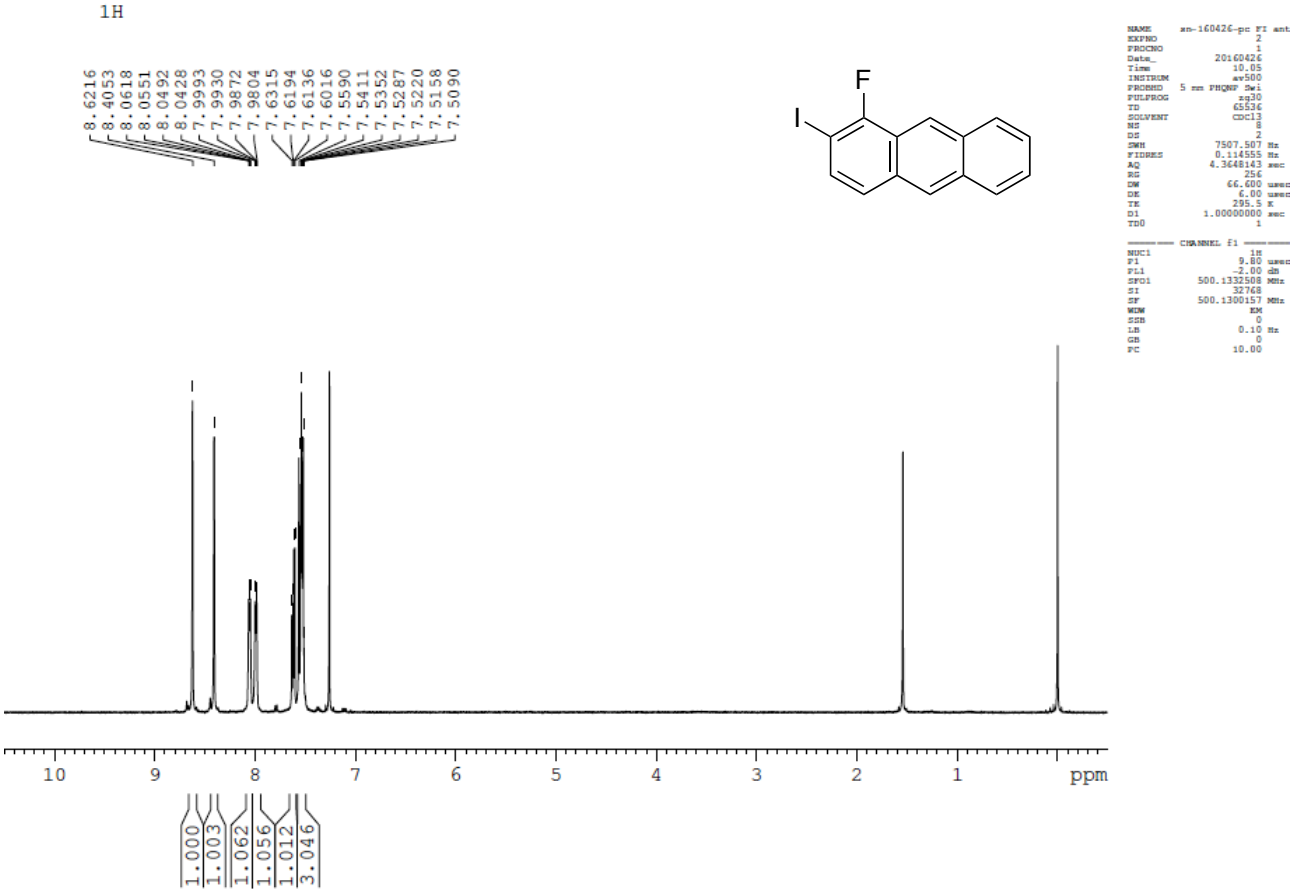
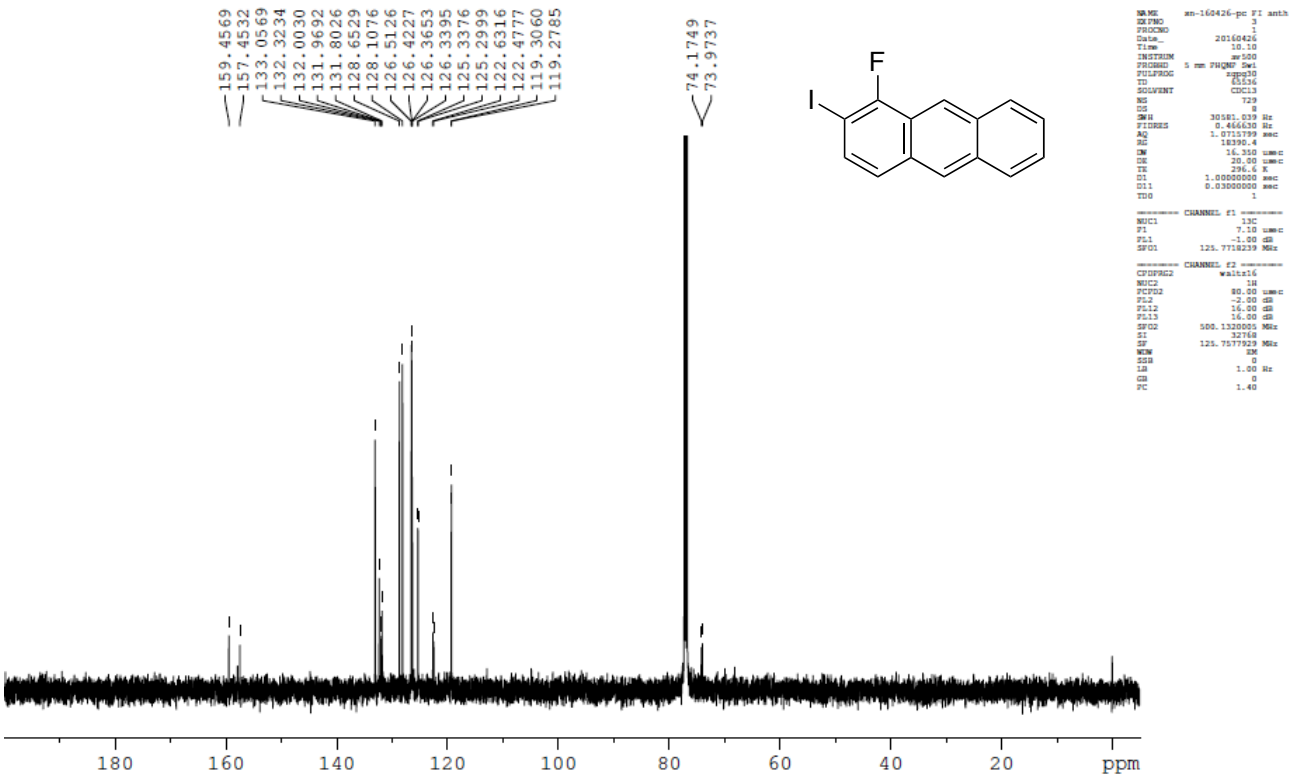
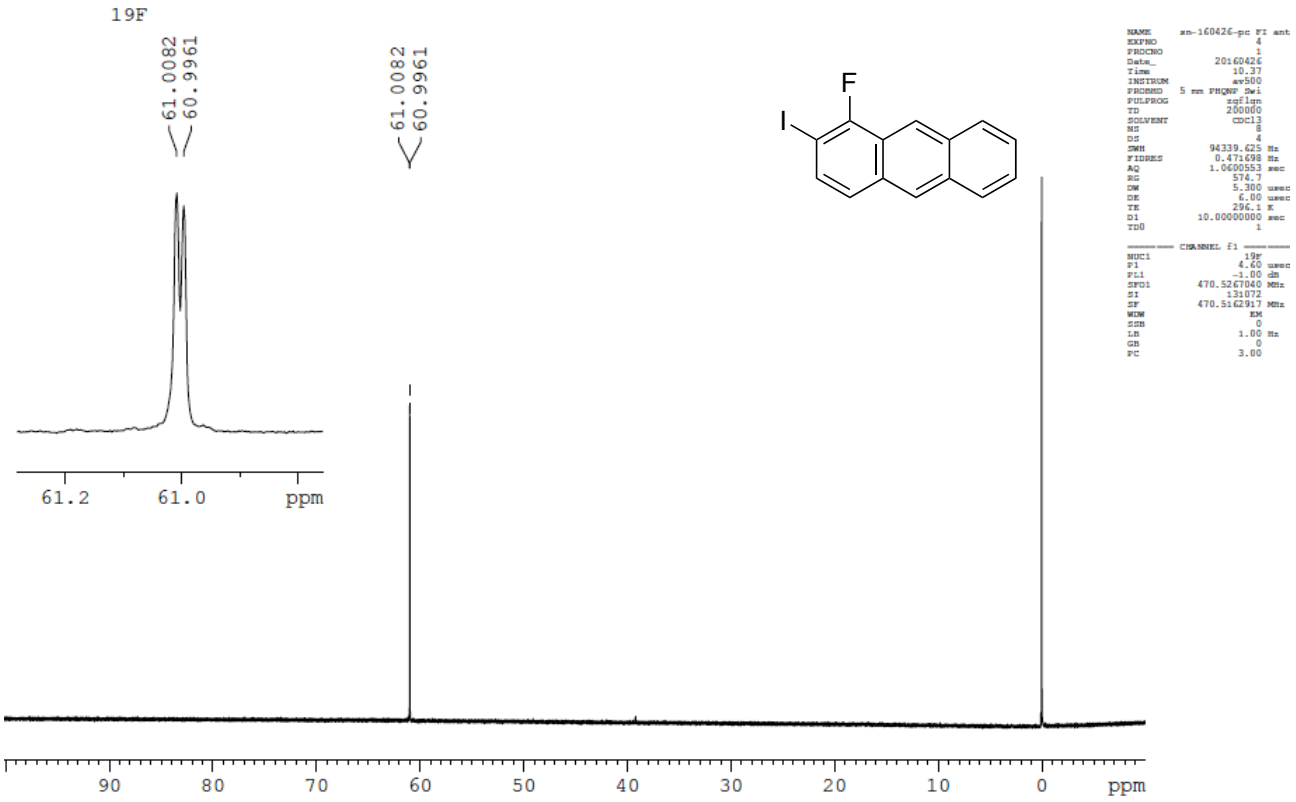
39.2420
39.2315
39.2647
39.2536
39.2420
39.2315
F
39.4
39.2
ppm
90
80
70
60
50
40
30
20
10
0
ppm

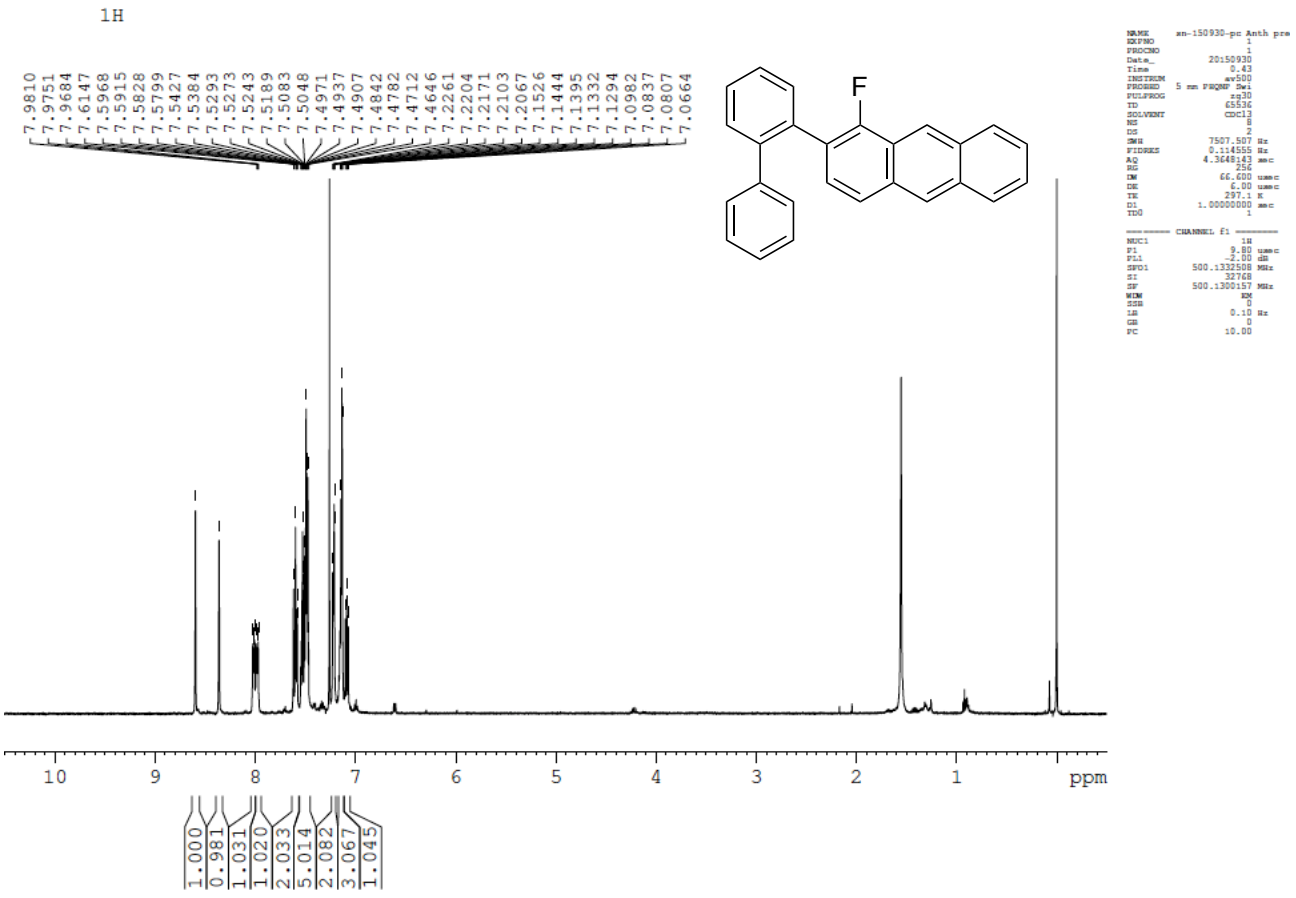
1-Fluoro-2-iodonaphthalene (4g)

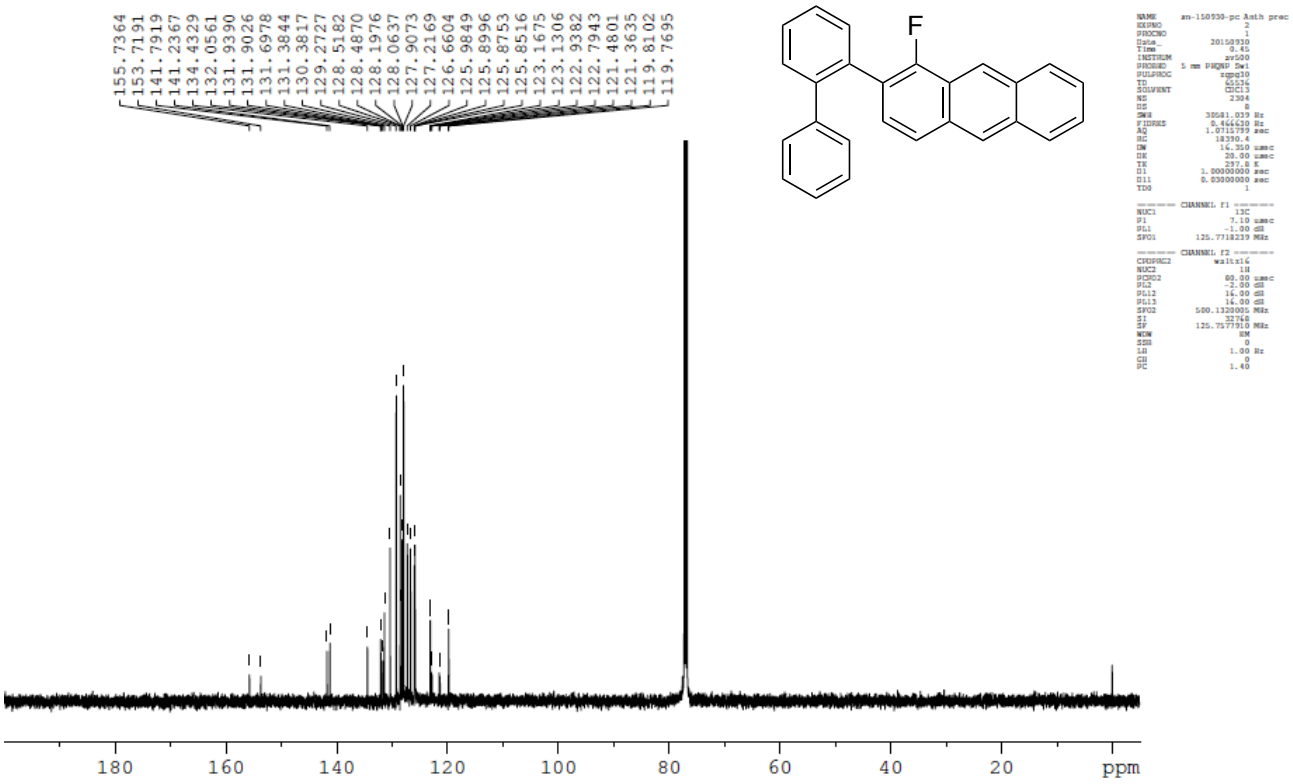






2-(Biphenyl-2-yl)-1-fluoroanthracene (1g)

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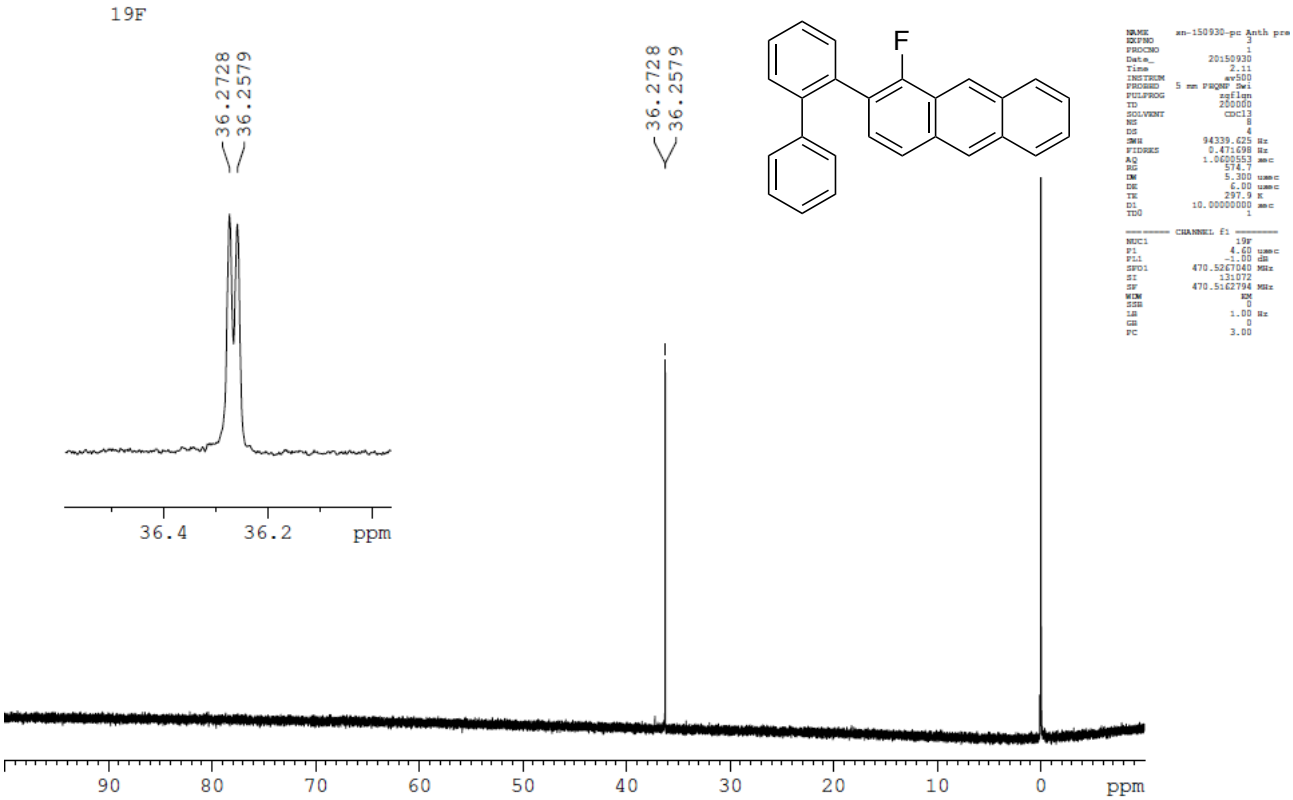
141.7919
141.2367
134.4329
132.0561
131.9390
131.9026
131.6978
131.3844
130.3817
129.2727
128.5182
128.4870
128.1976
128.0637
127.9073
127.2169
126.6604
125.9849
125.8996
125.8753
125.8516
123.1675
123.1306
122.9382
122.7943
121.4801
121.3635
119.8102
119.7695
F
180
160
140
120
100
80
60
40
20
ppm


19F
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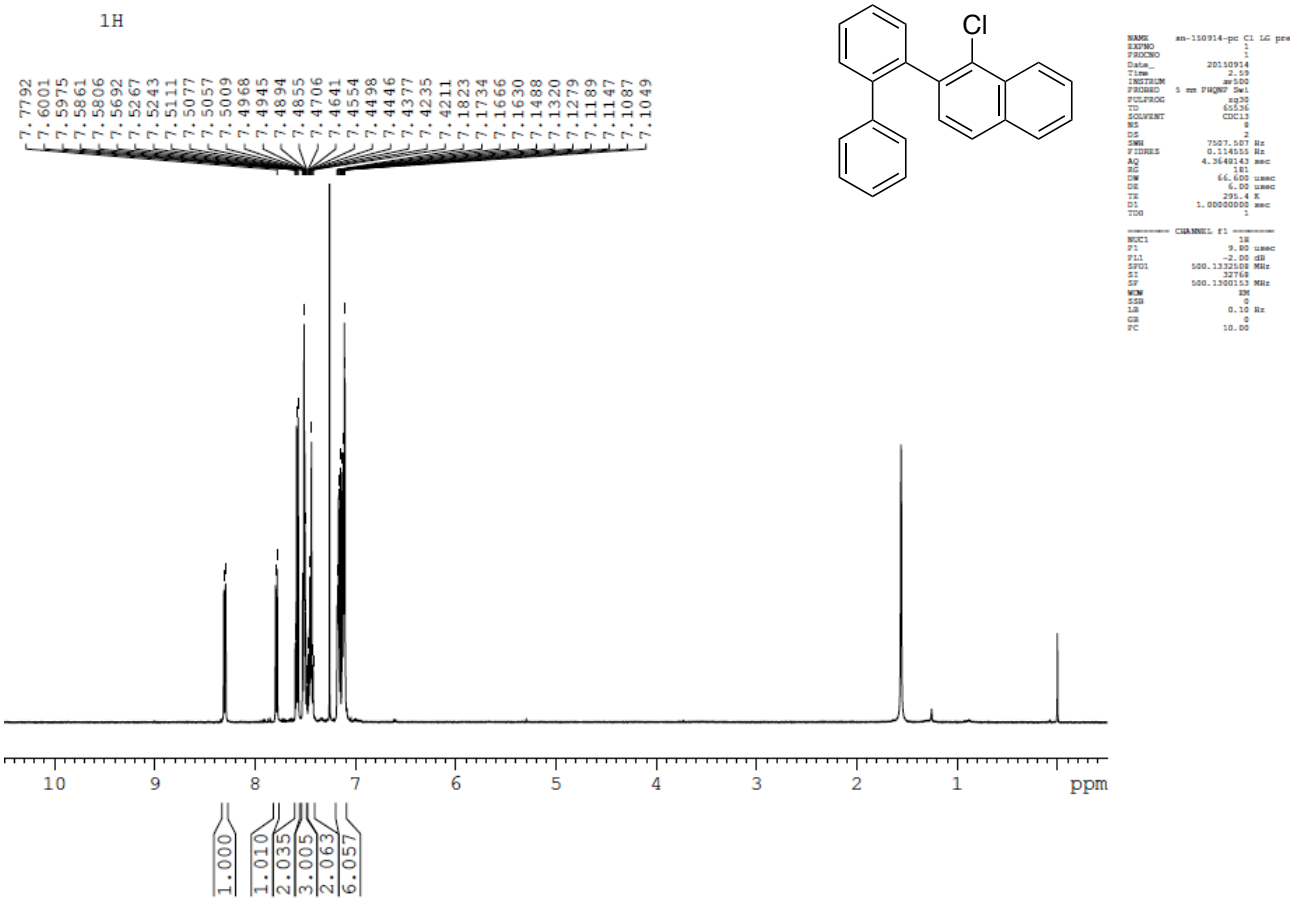
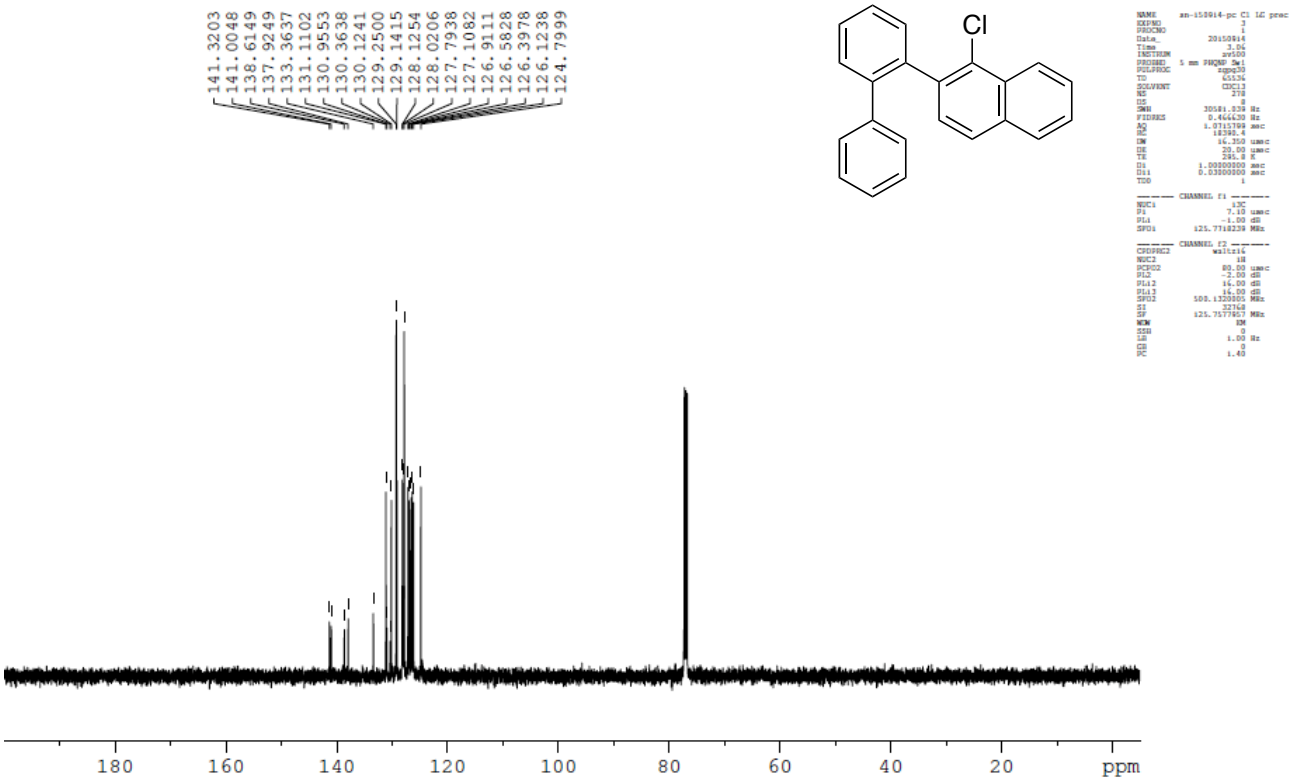
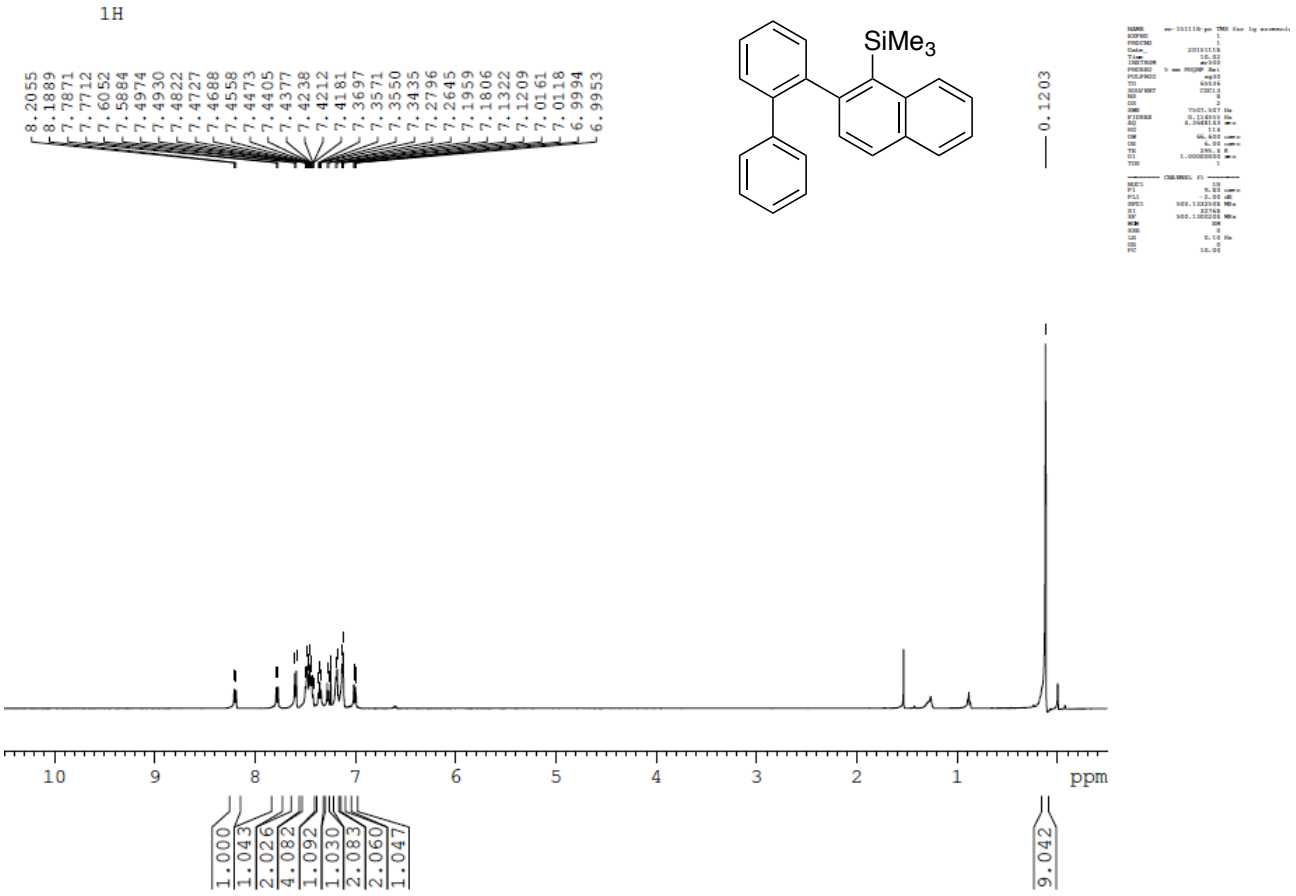
36.2728
36.2579
F
36.4
36.2
ppm
90
80
70
60
50
40
30
20
10
0
ppm

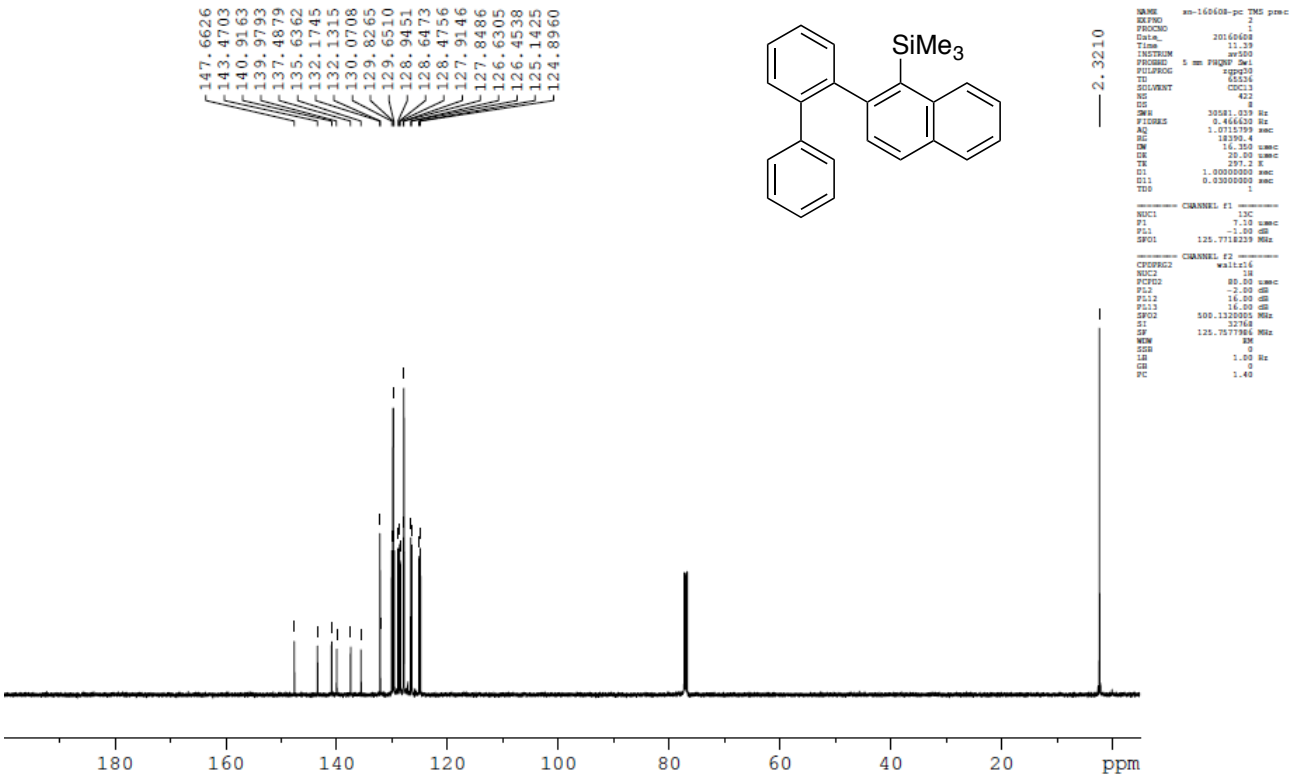
2-(Biphenyl-2-yl)-1-chloronaphthalene (1h)



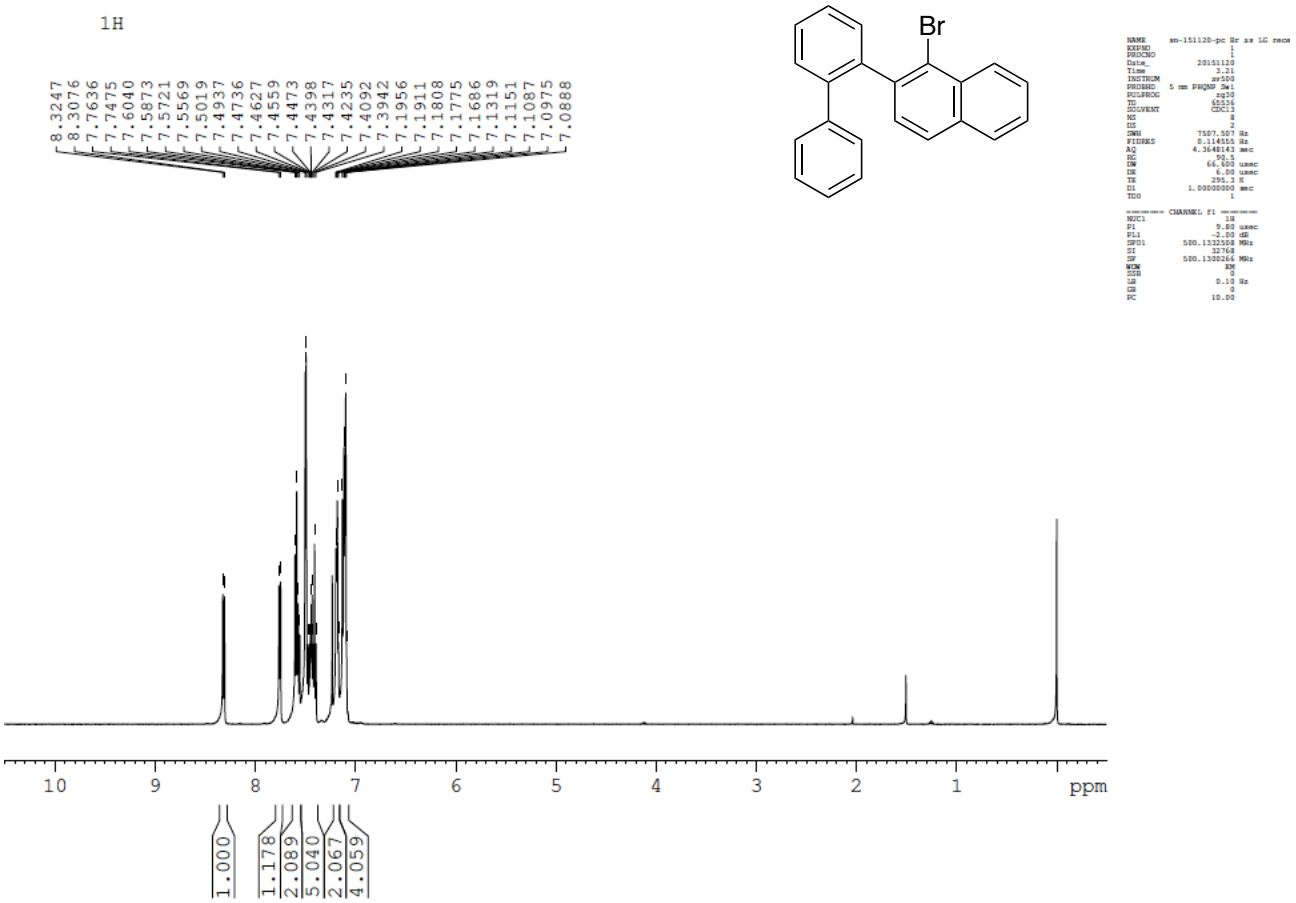


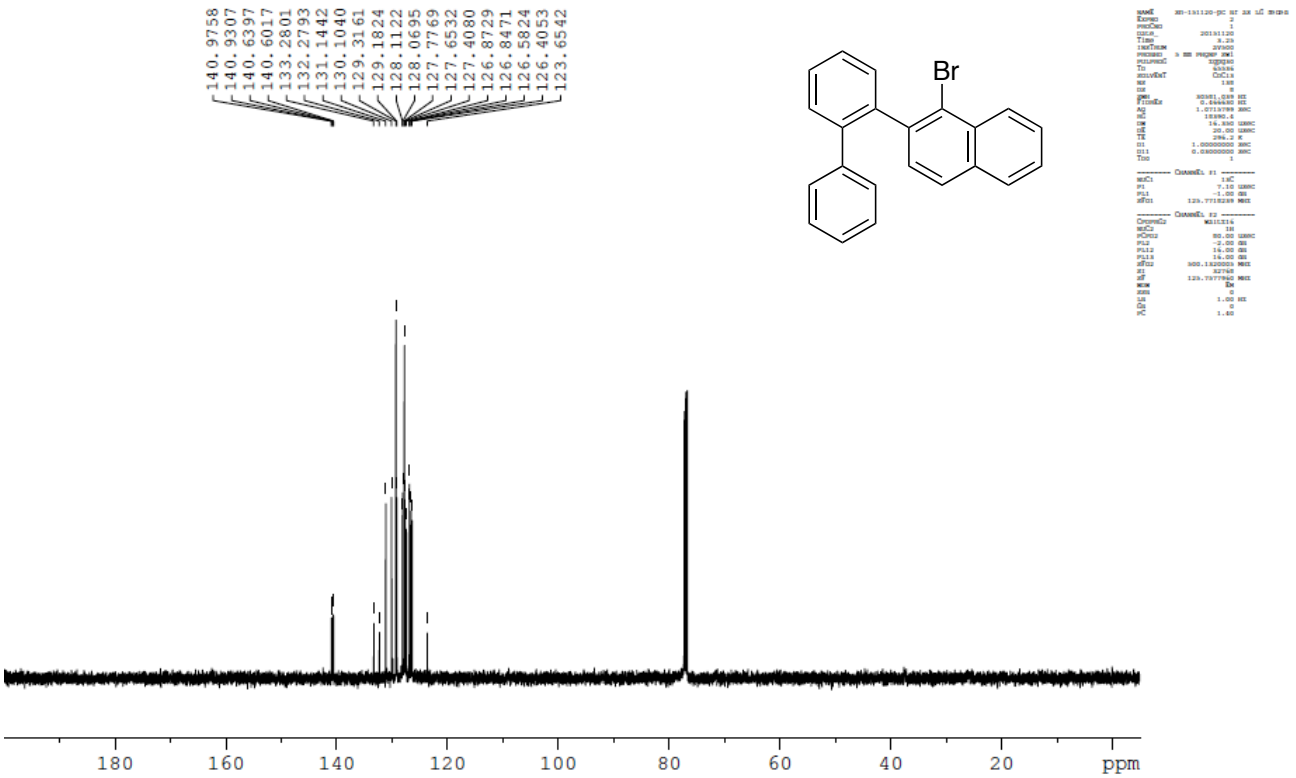
[2-(Biphenyl-2-yl)naphthalen-1-yl]trimethylsilane



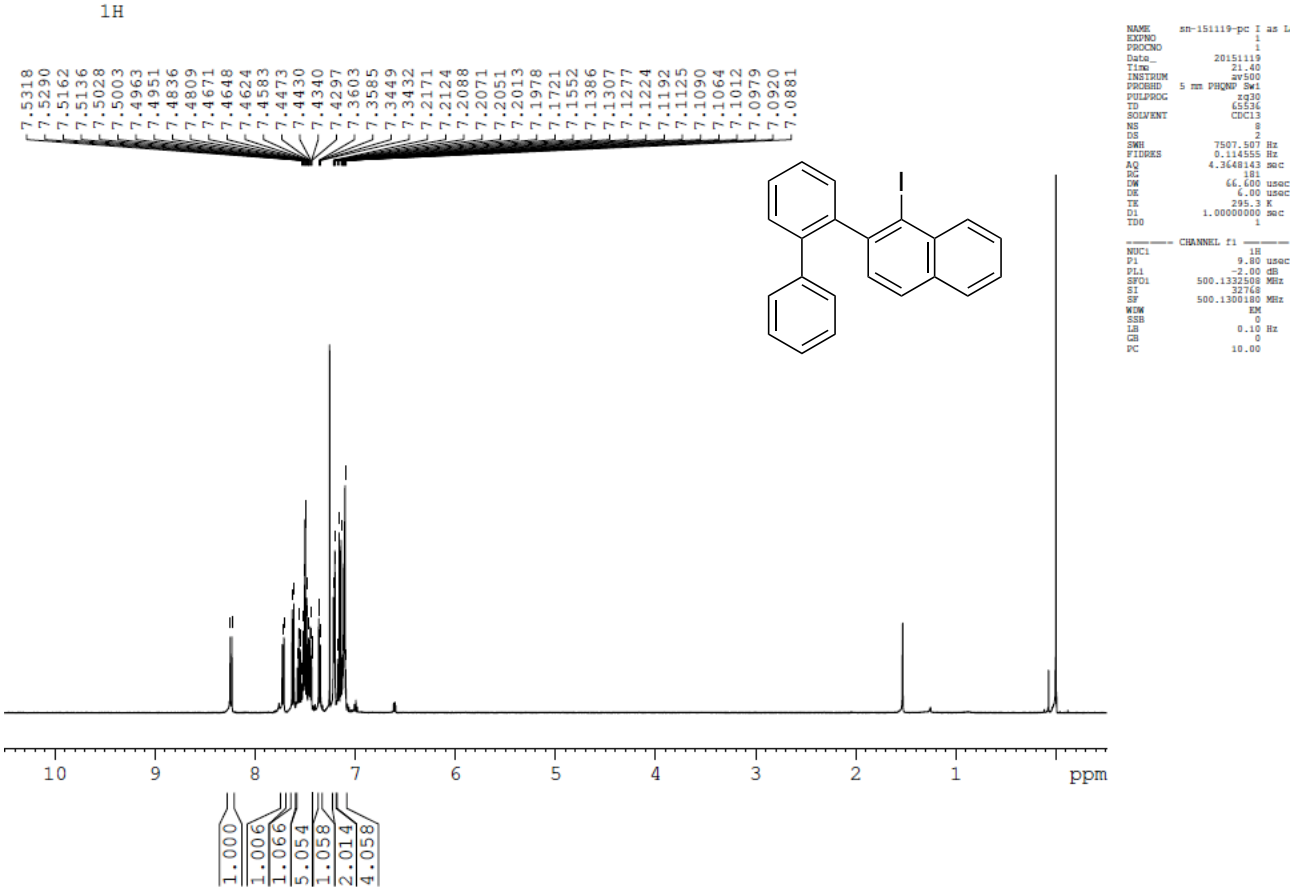


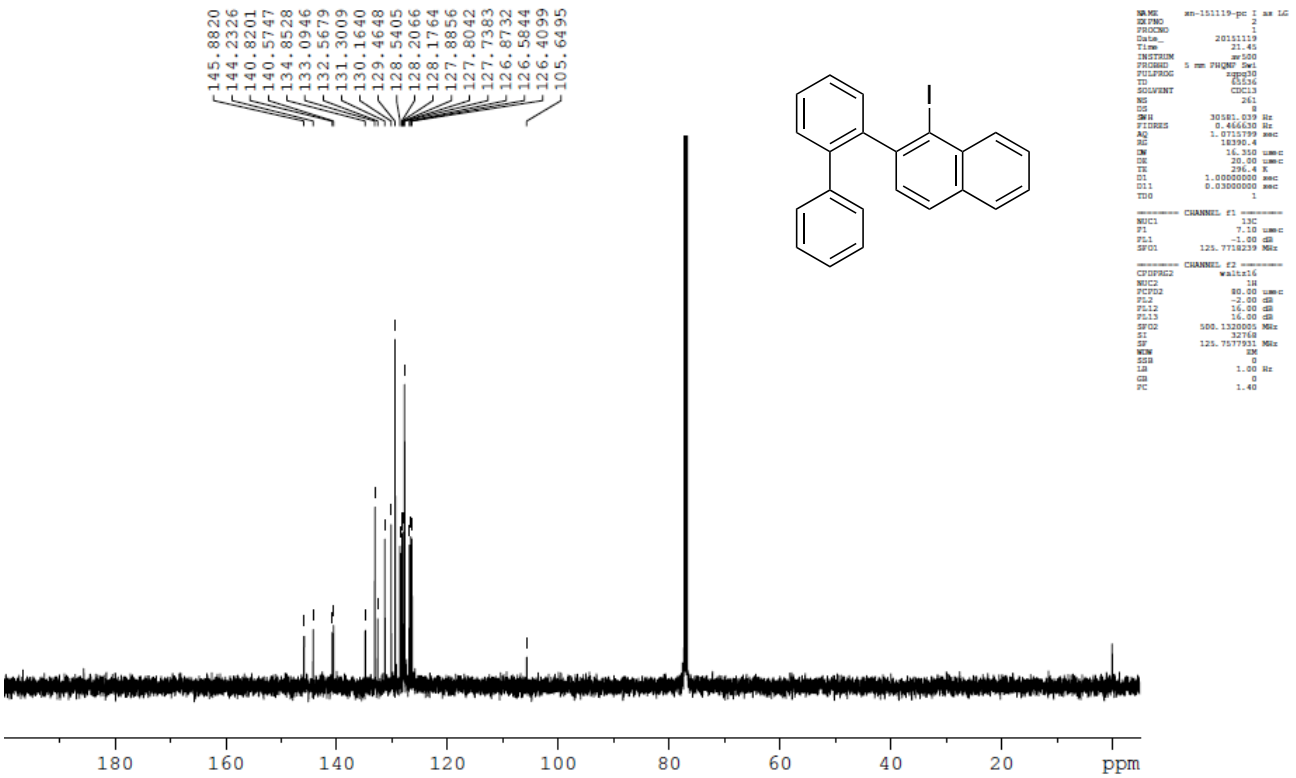
2-(Biphenyl-2-yl)-1-bromonaphthalene (1i)



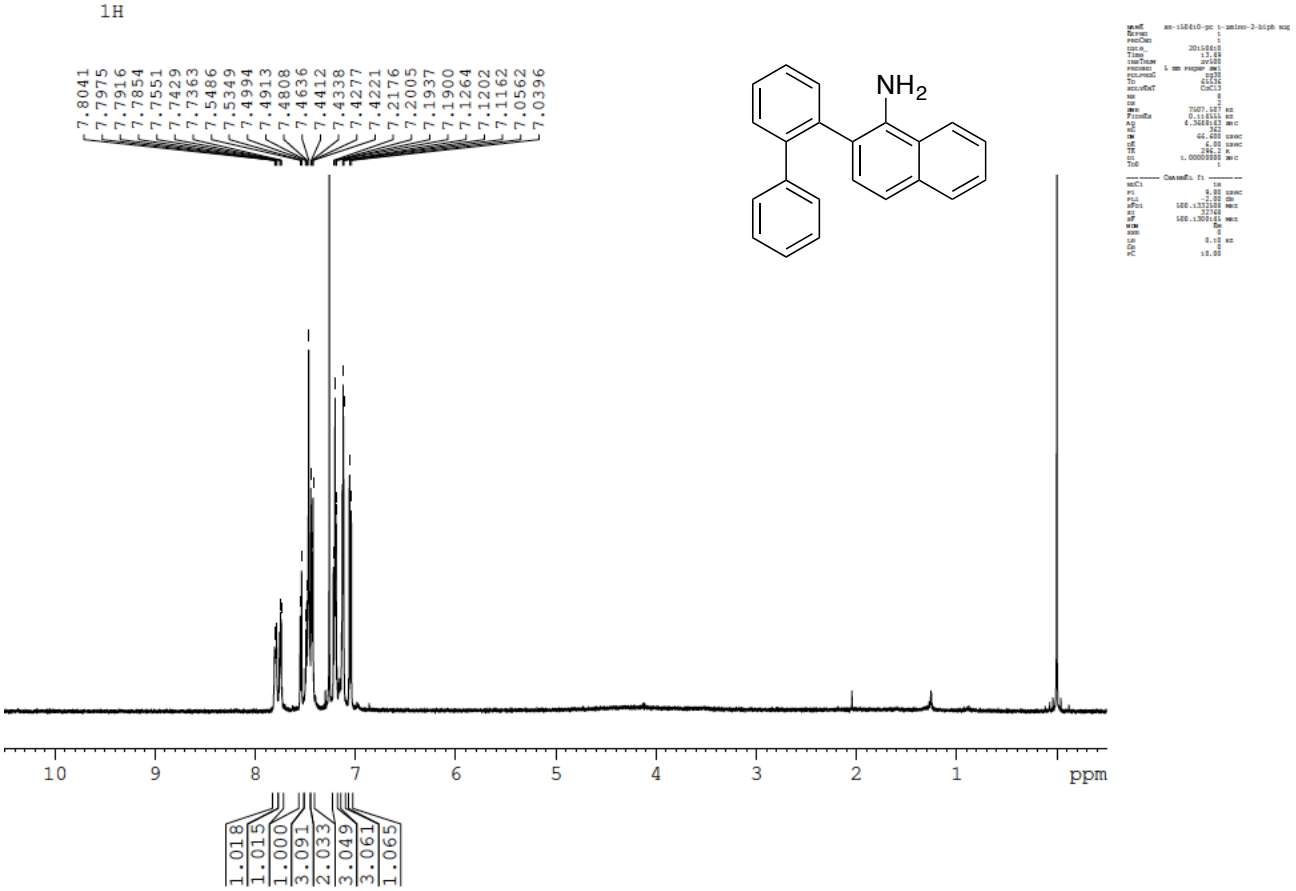


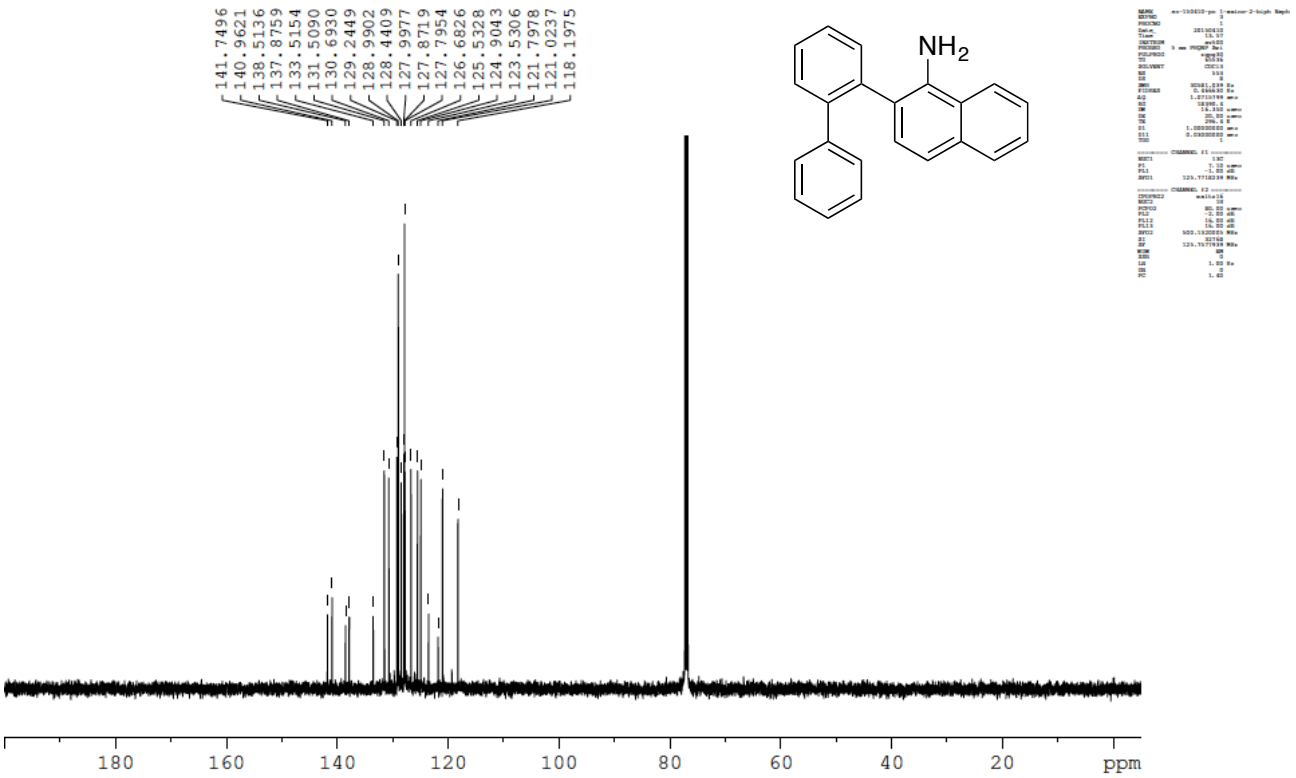
2-(Biphenyl-2-yl)-1-iodonaphthalene (1j)



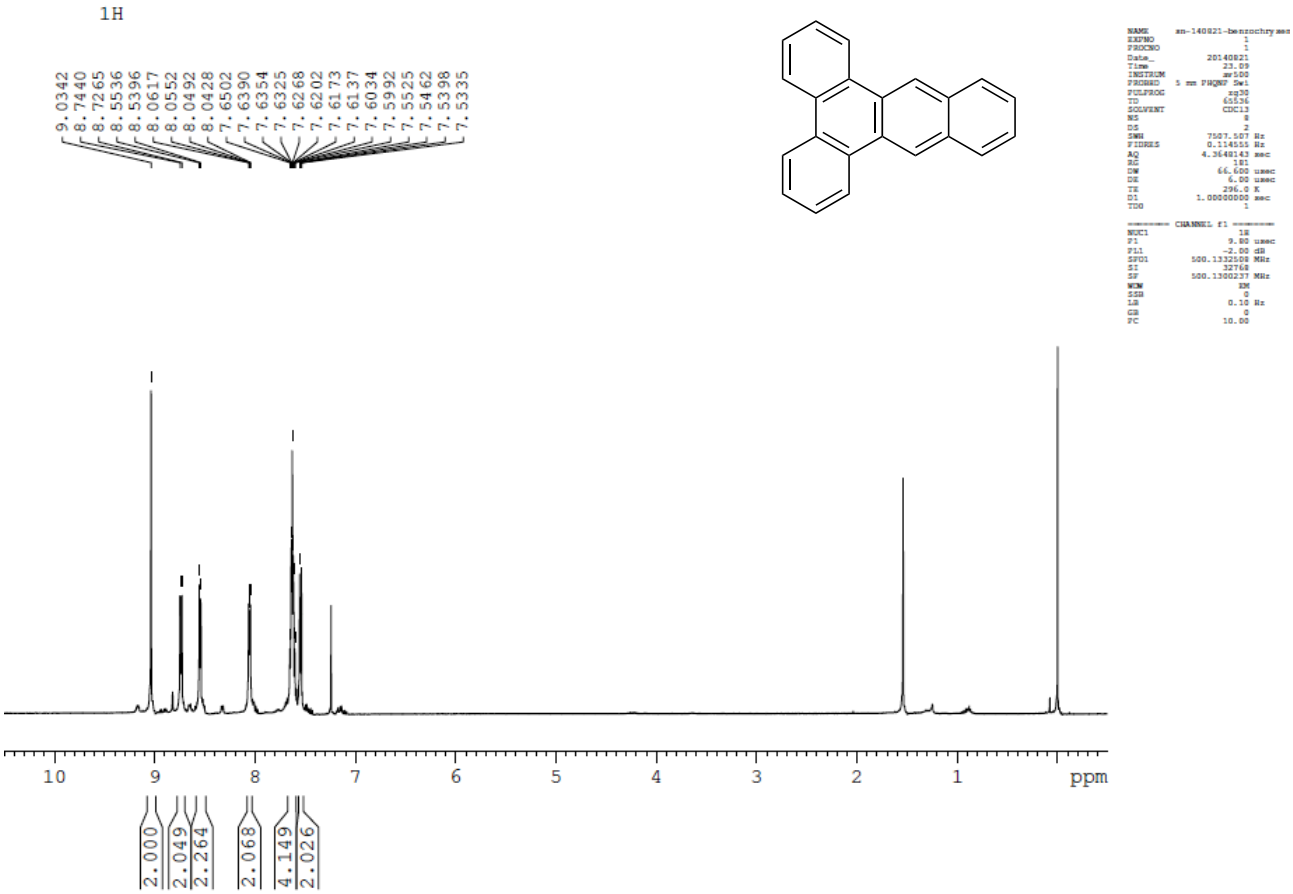


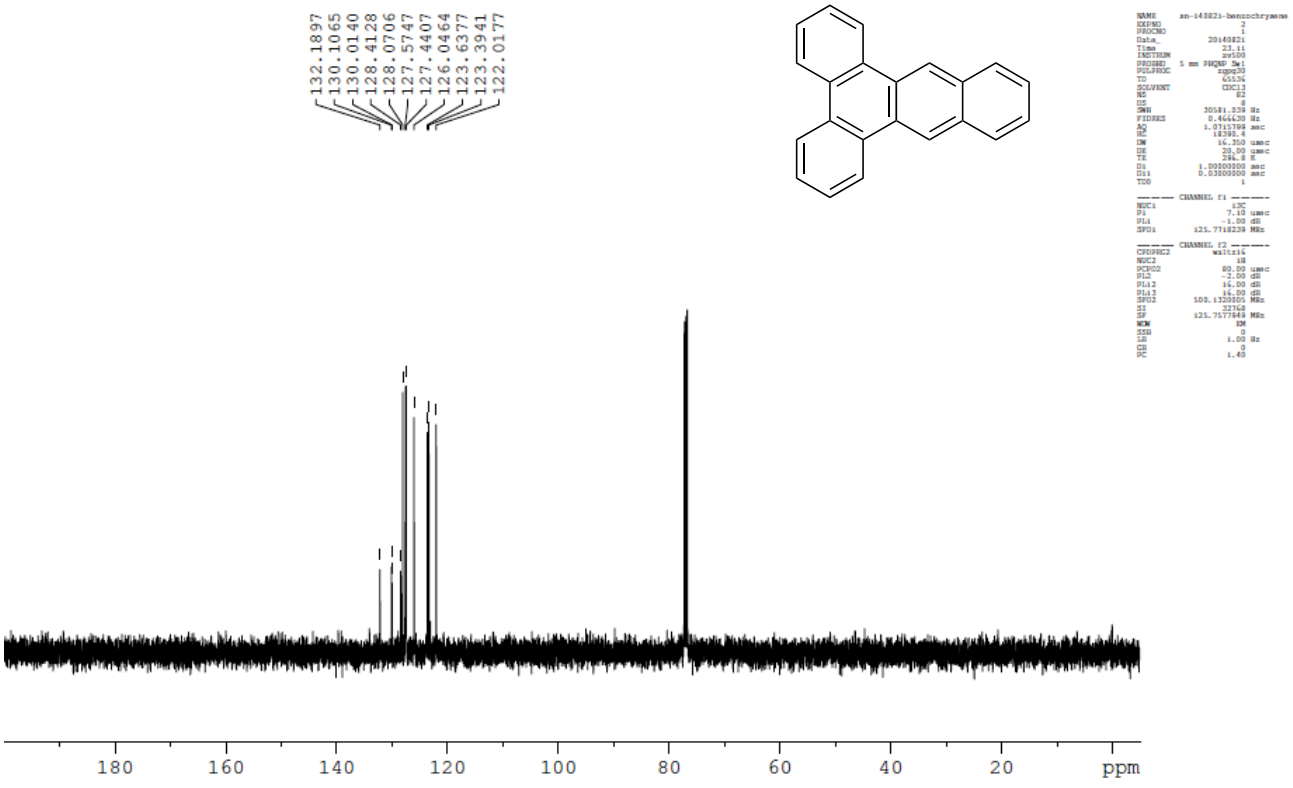
2-(Biphenyl-2-yl)naphthalen-1-amine (1k)



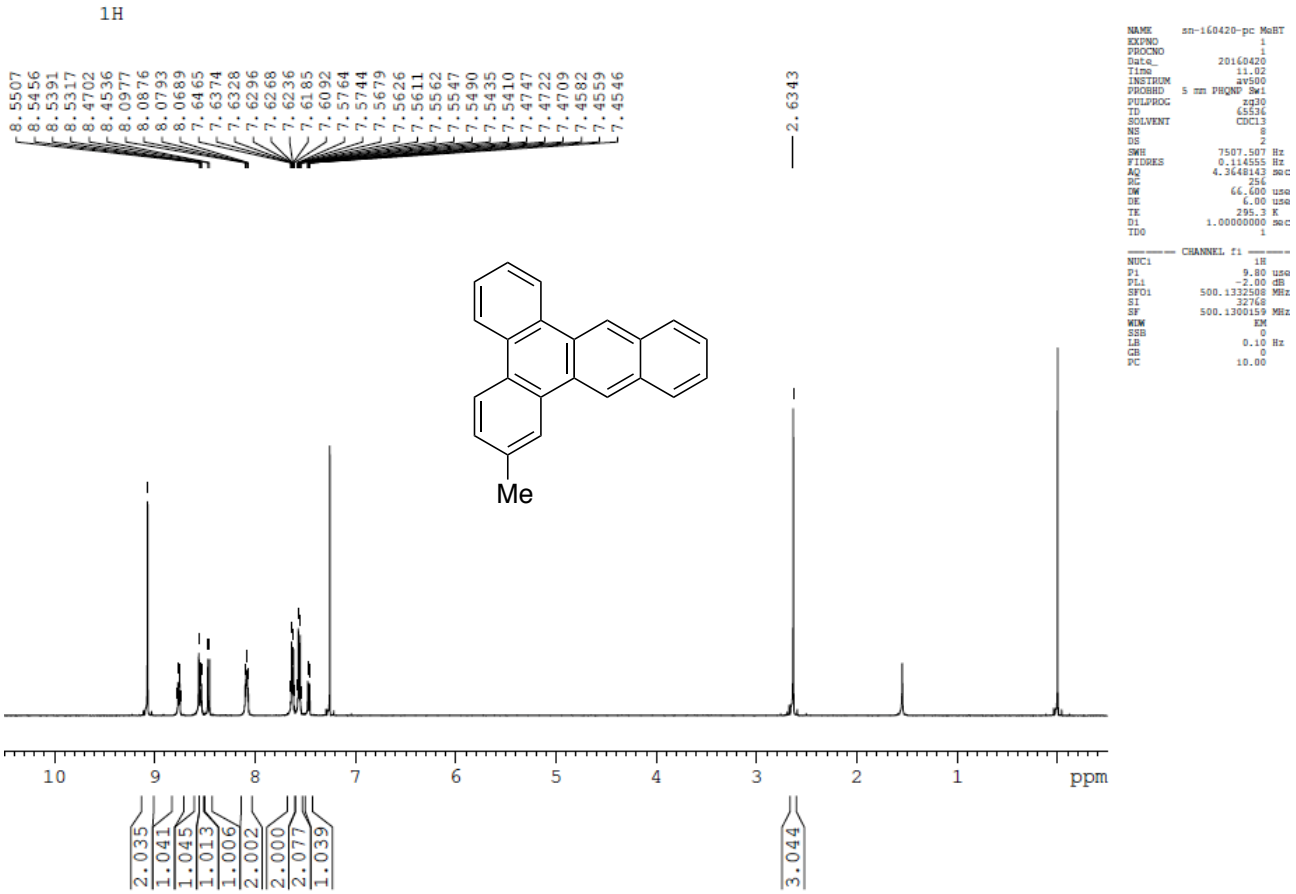


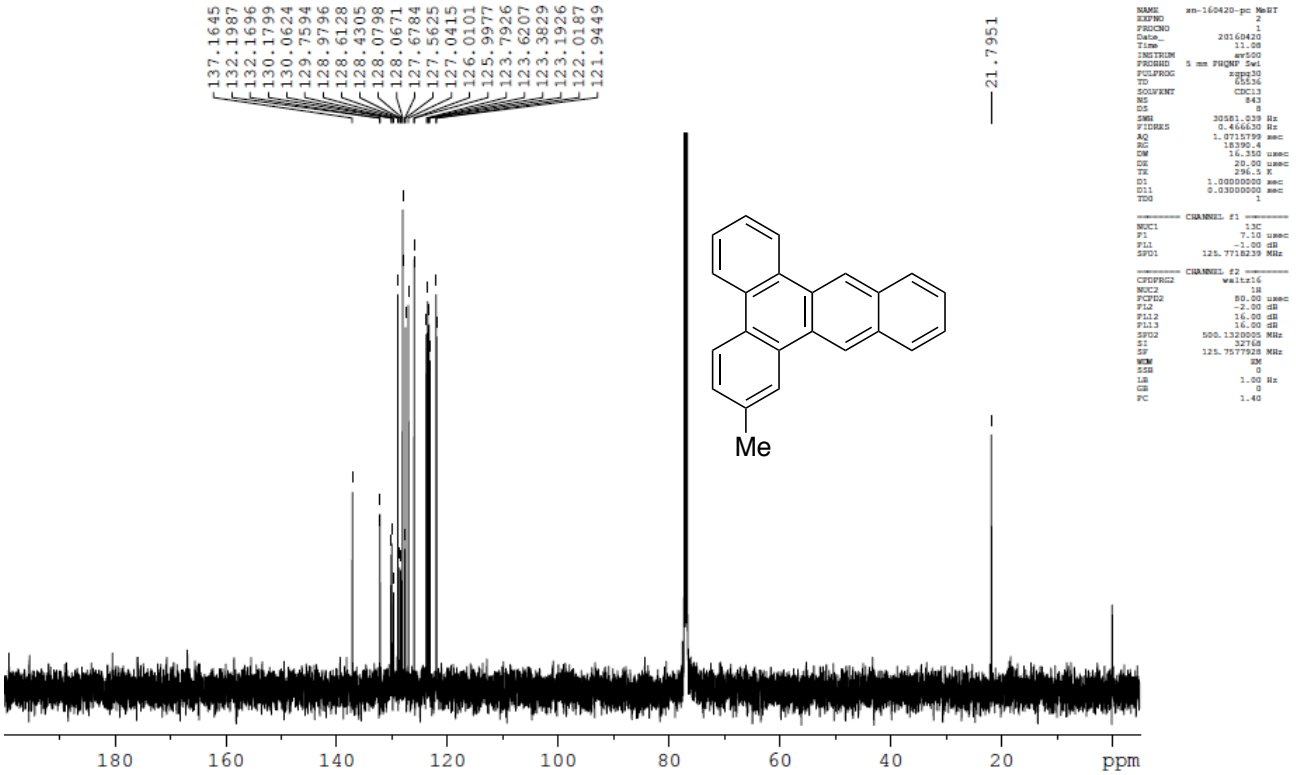
Benzo[*f*]tetraphene (2a)



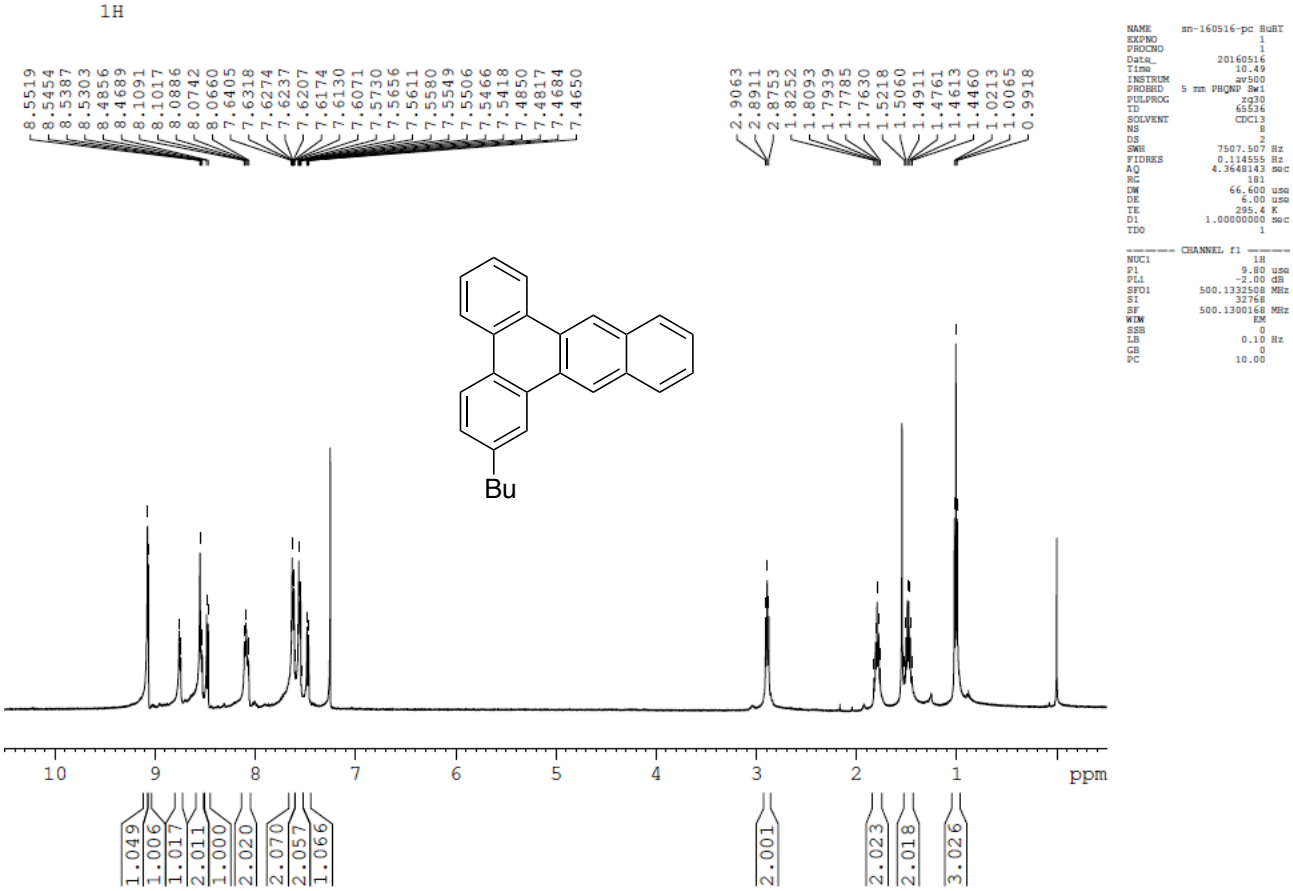


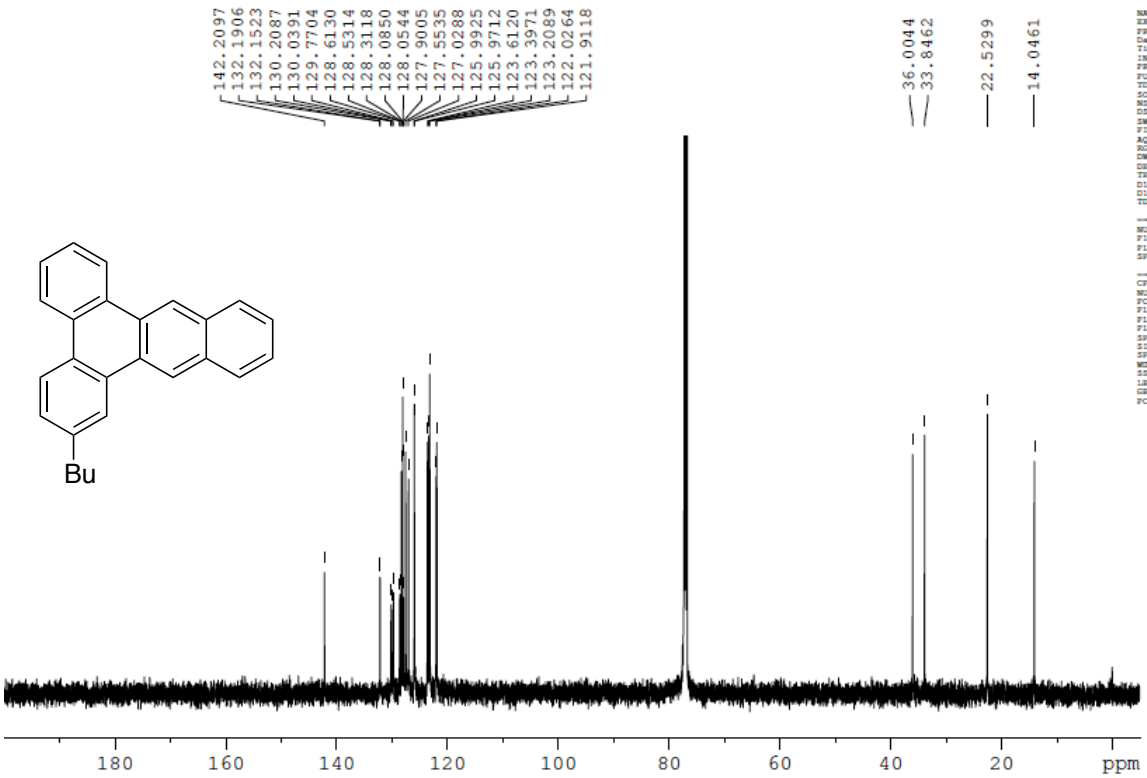
2-Methylbenzo[*f*]tetraphene (2b)



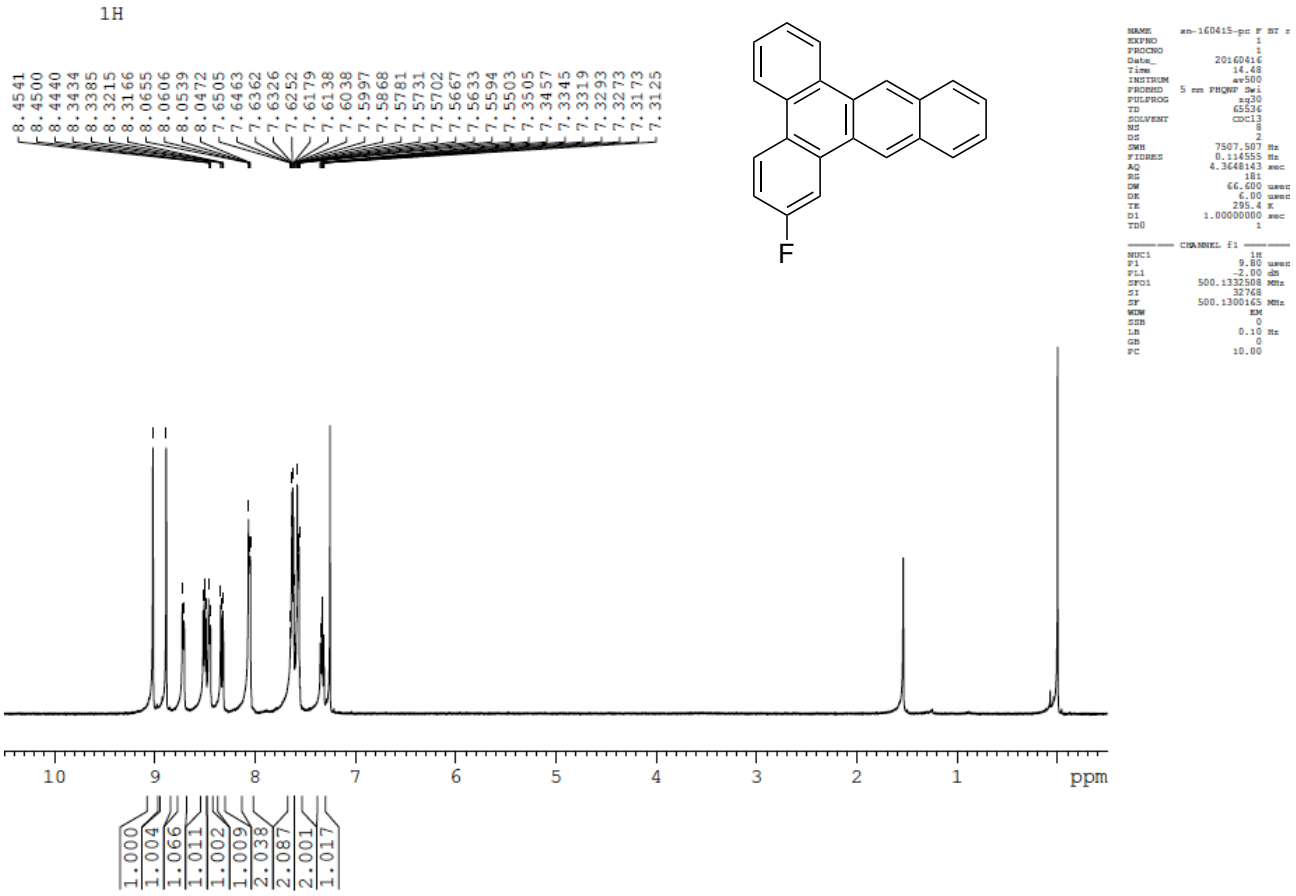


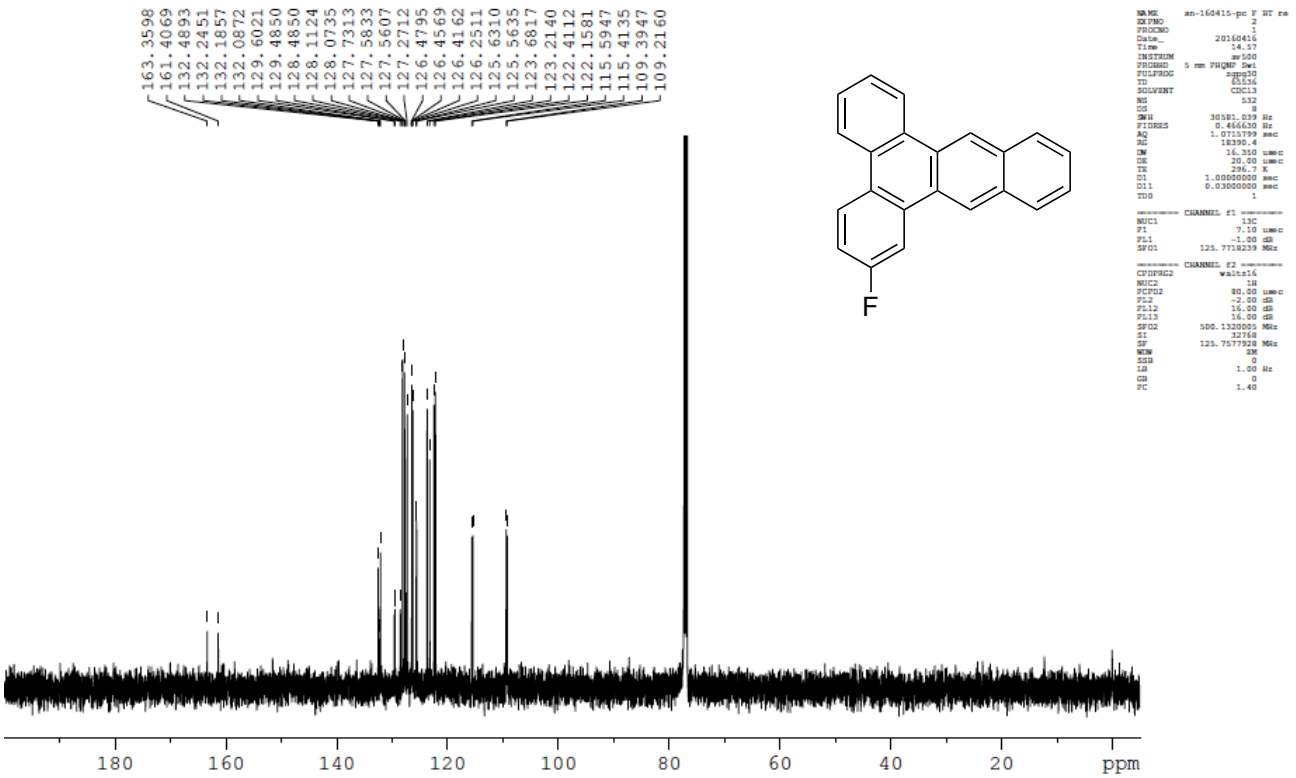
2-Butylbenzo[*f*]tetraphene (2c)

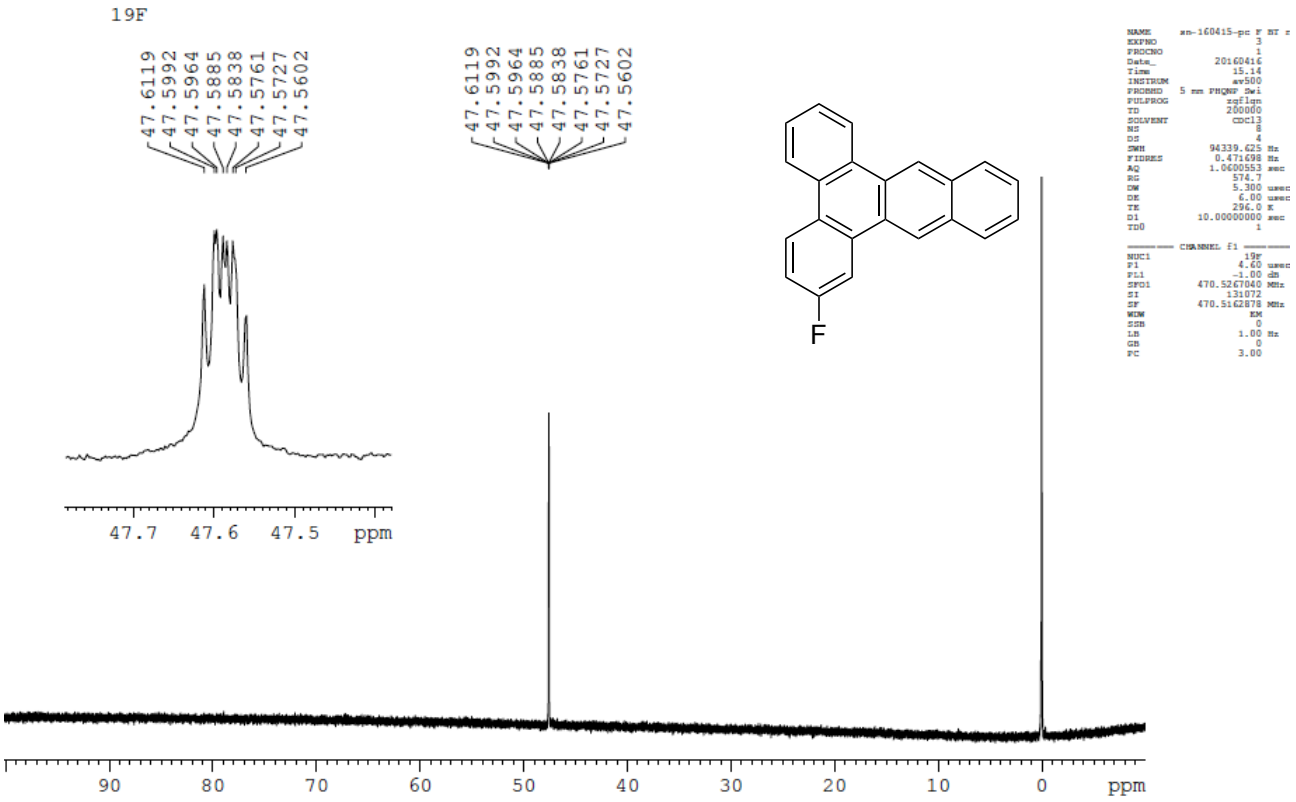




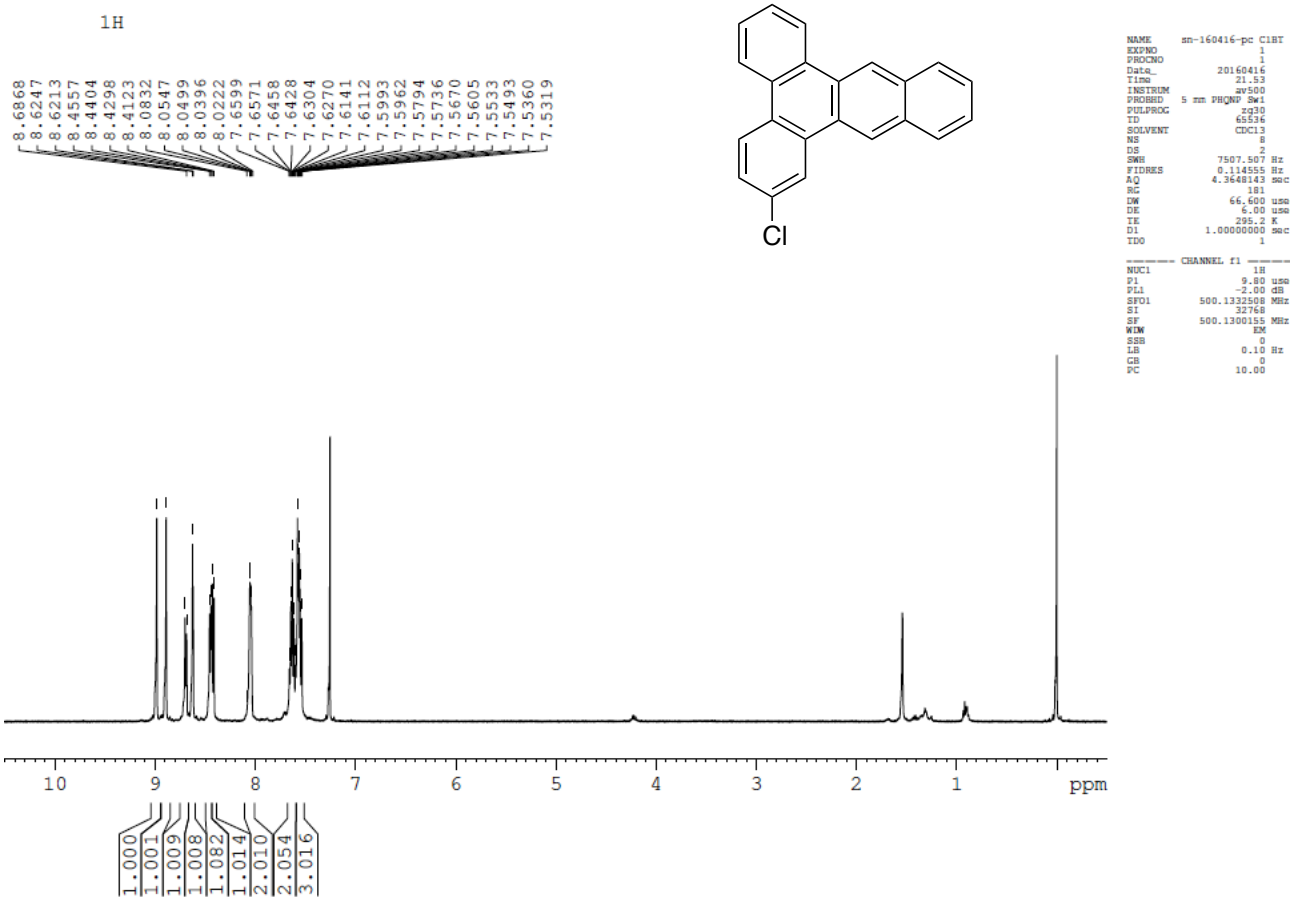
2-Fluorobenzo[*f*]tetraphene (2d)

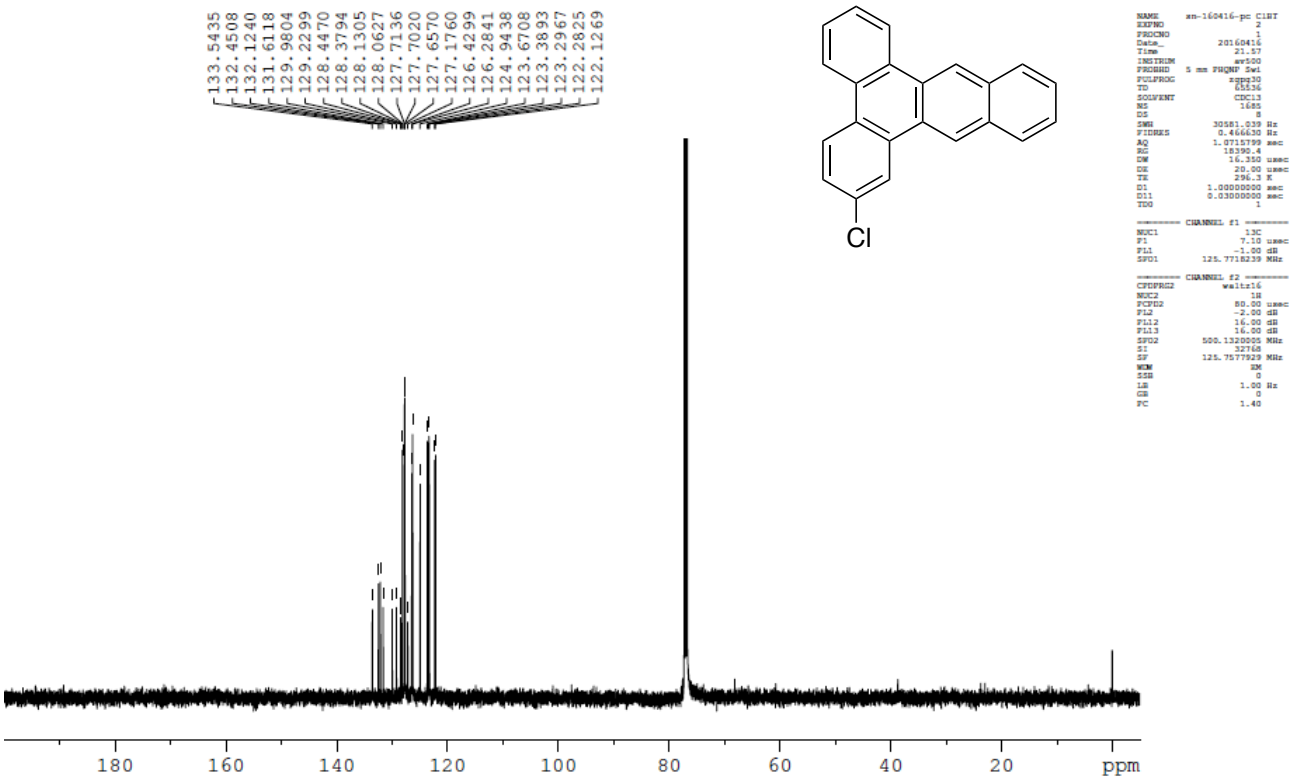




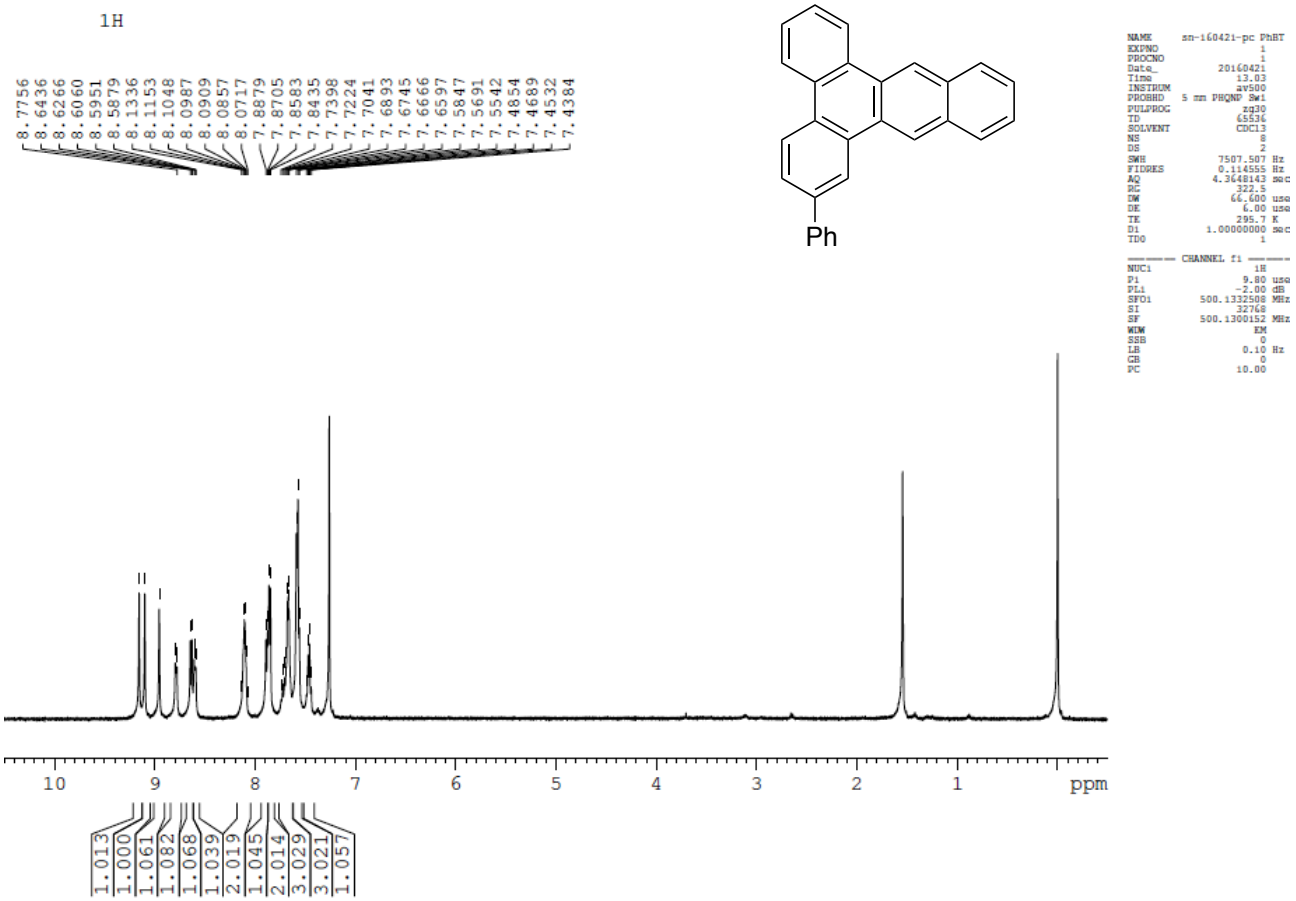


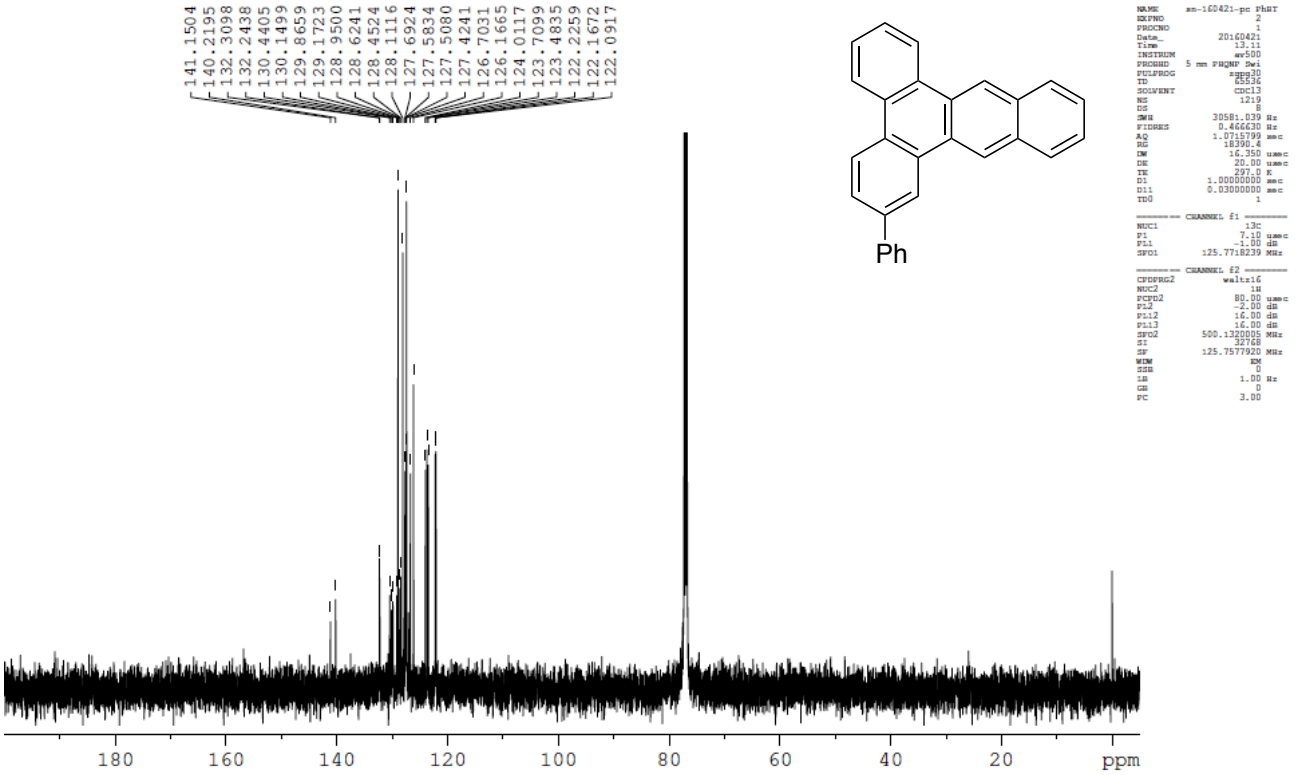
2-Chlorobenzo[*f*]tetraphene (2e)



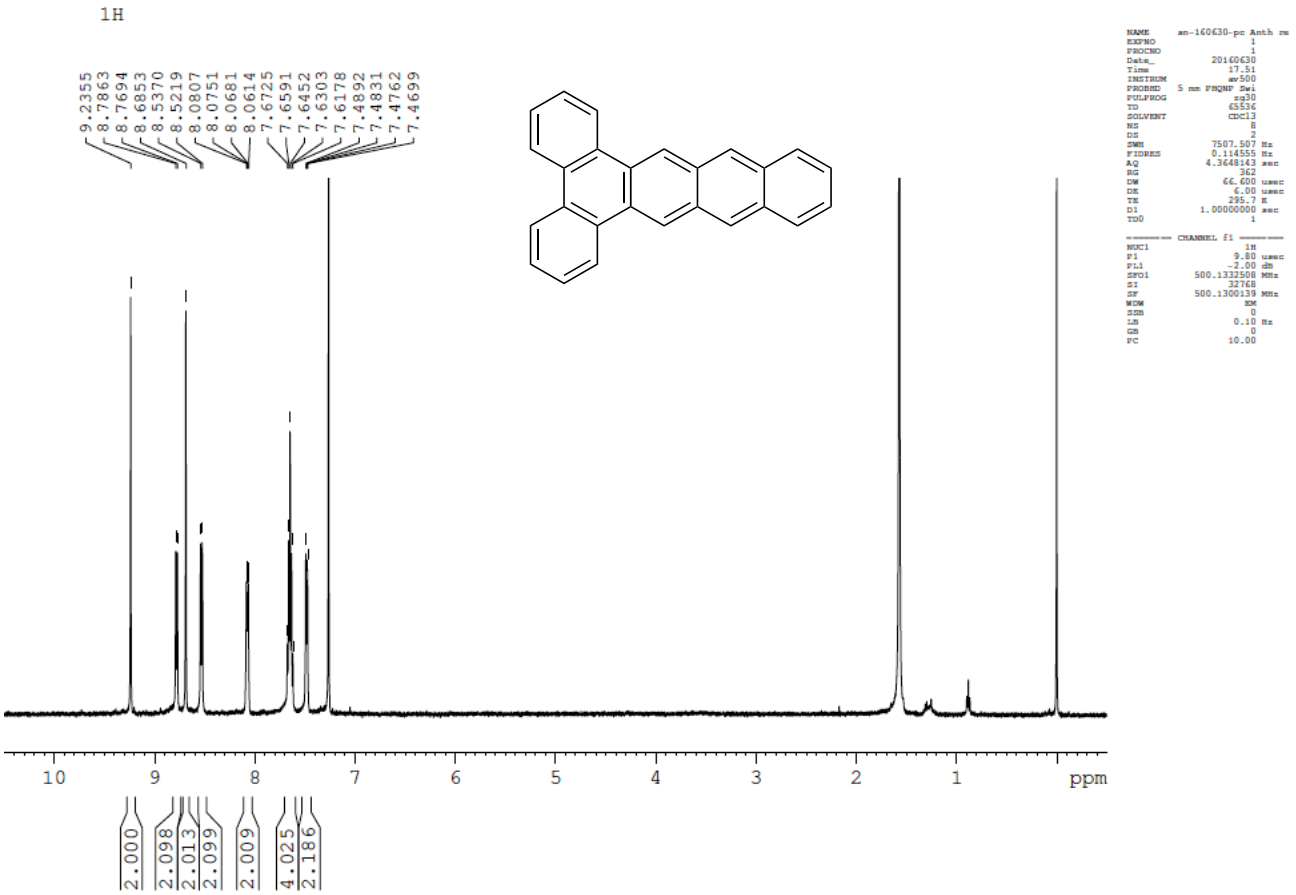


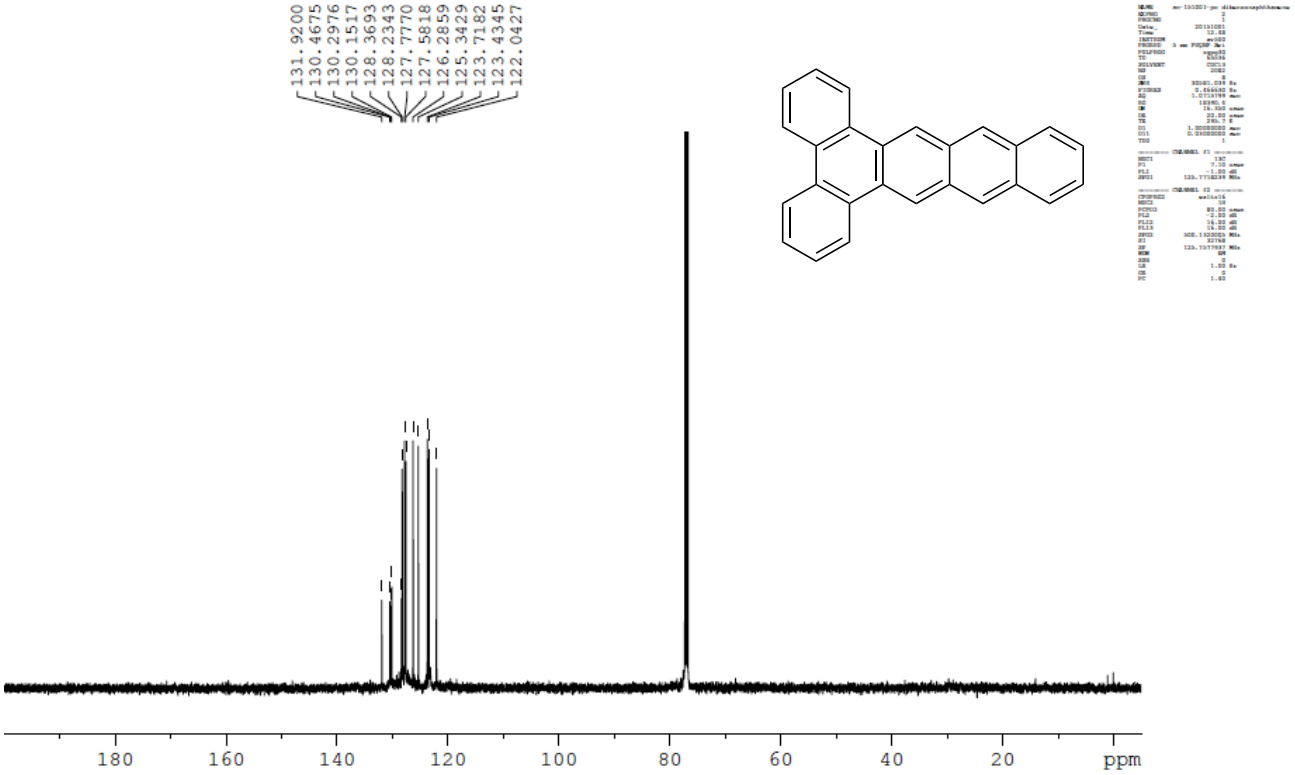
2-Phenylbenzo[*f*]tetraphene (2f)



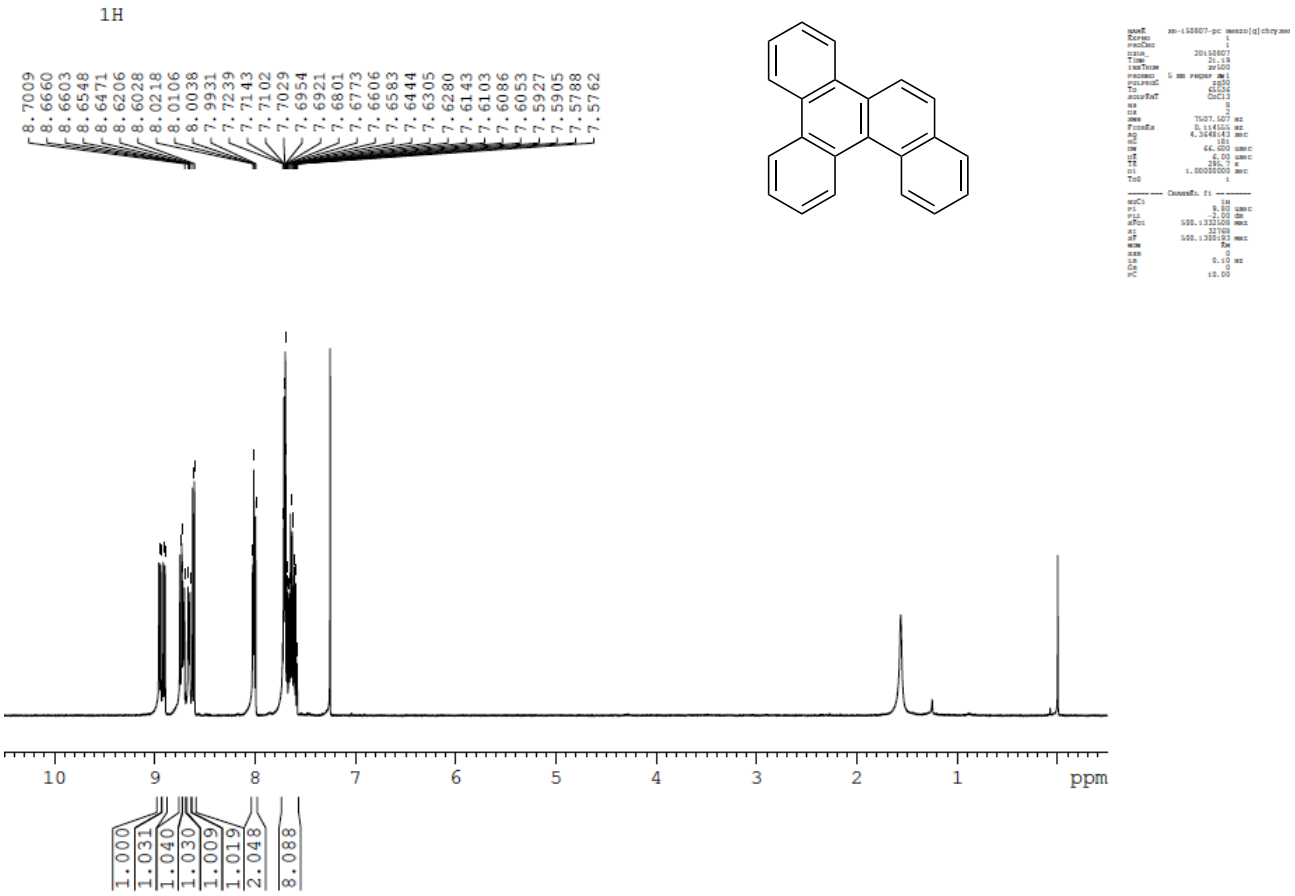


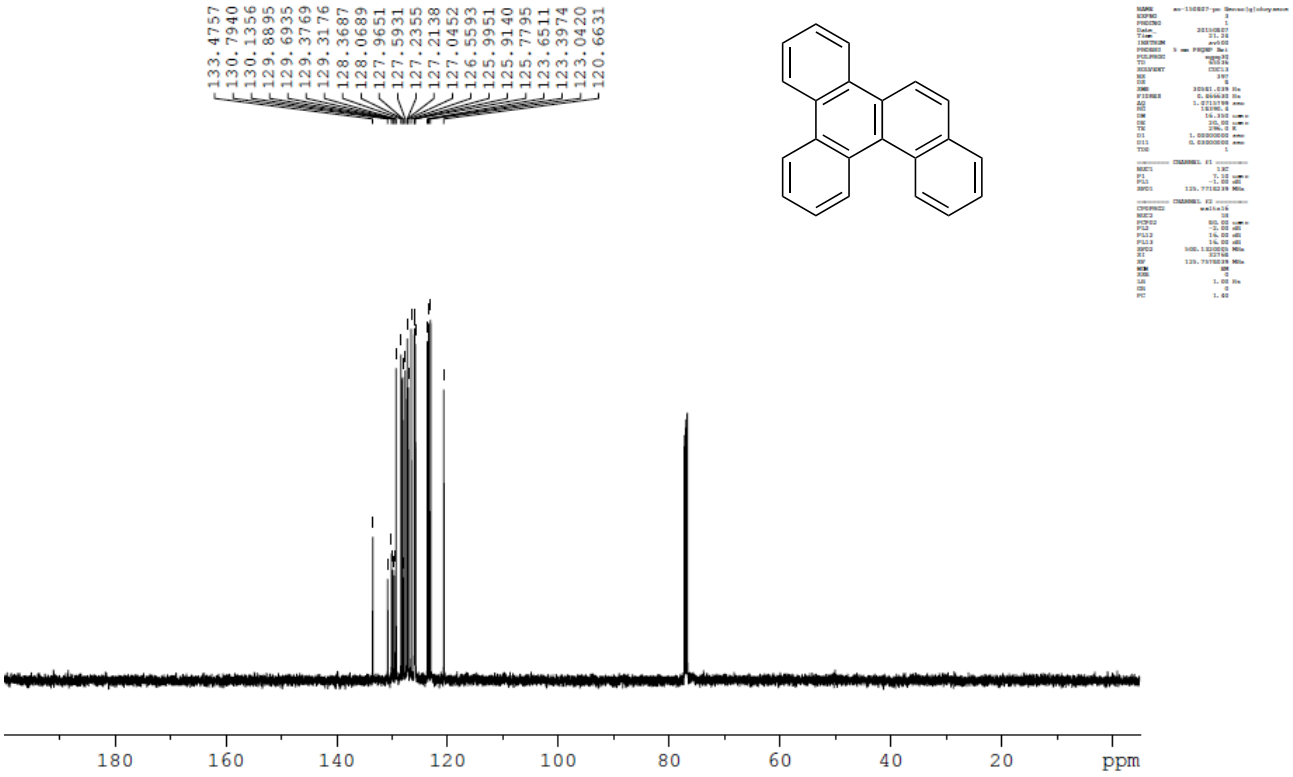
Dibenzo[*a*,*c*]tetracene (2g)



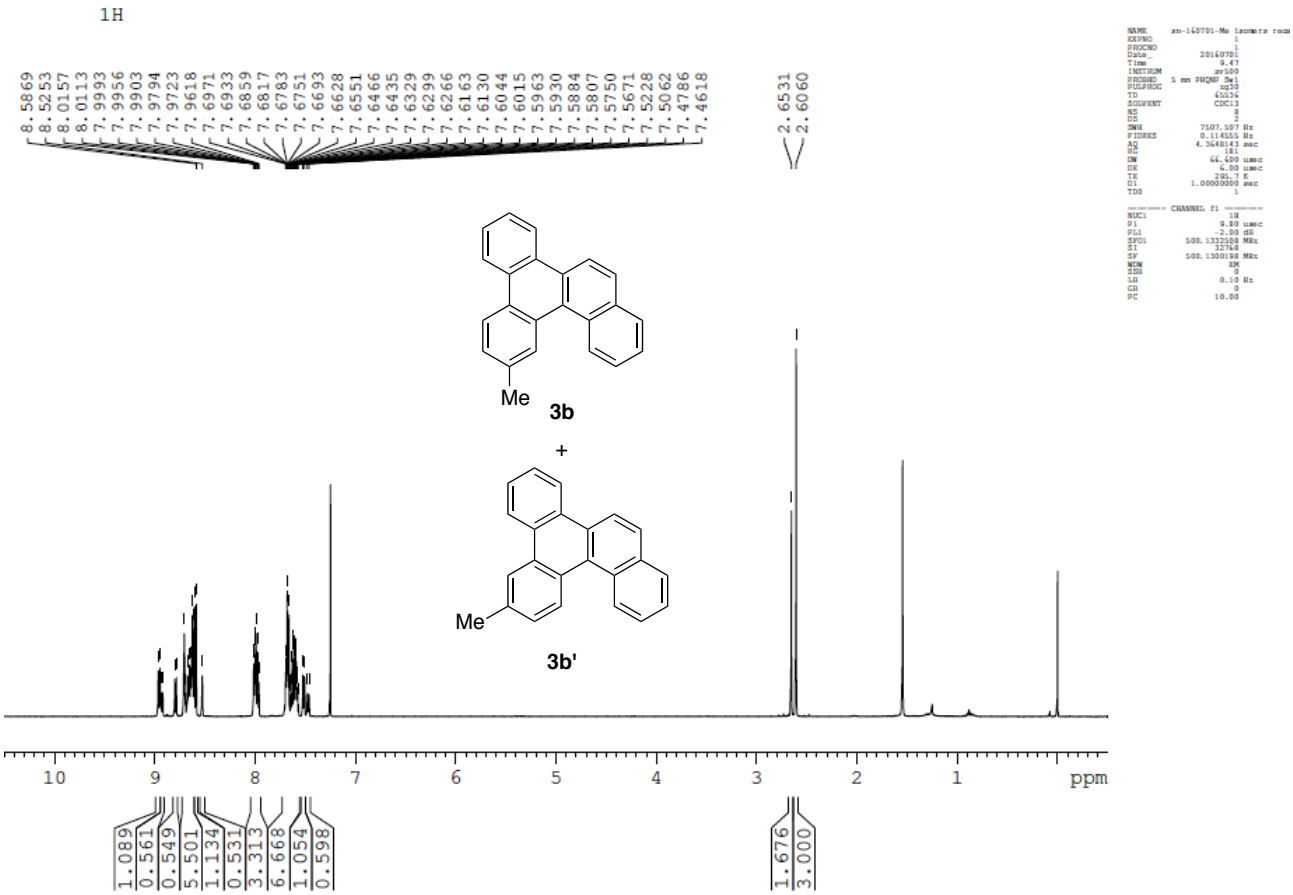


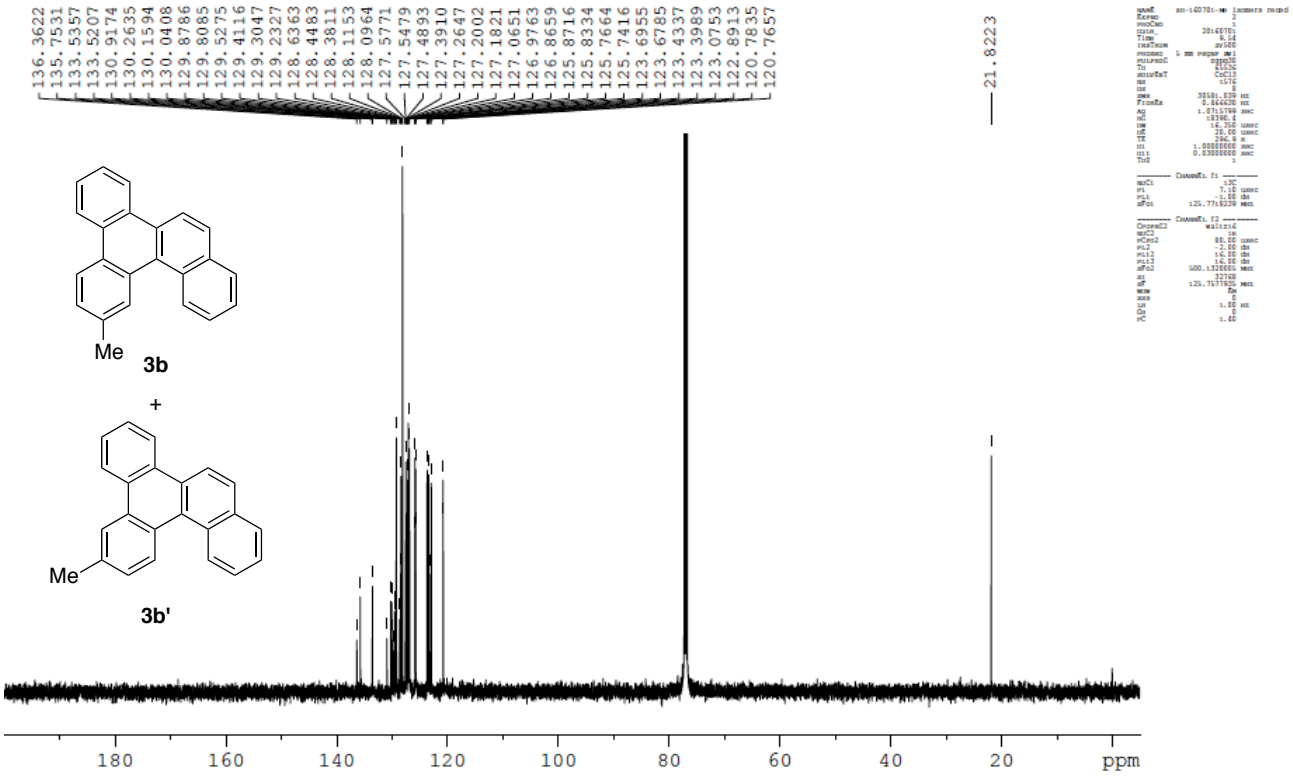
Benzo[*g*]chrysene (3a)



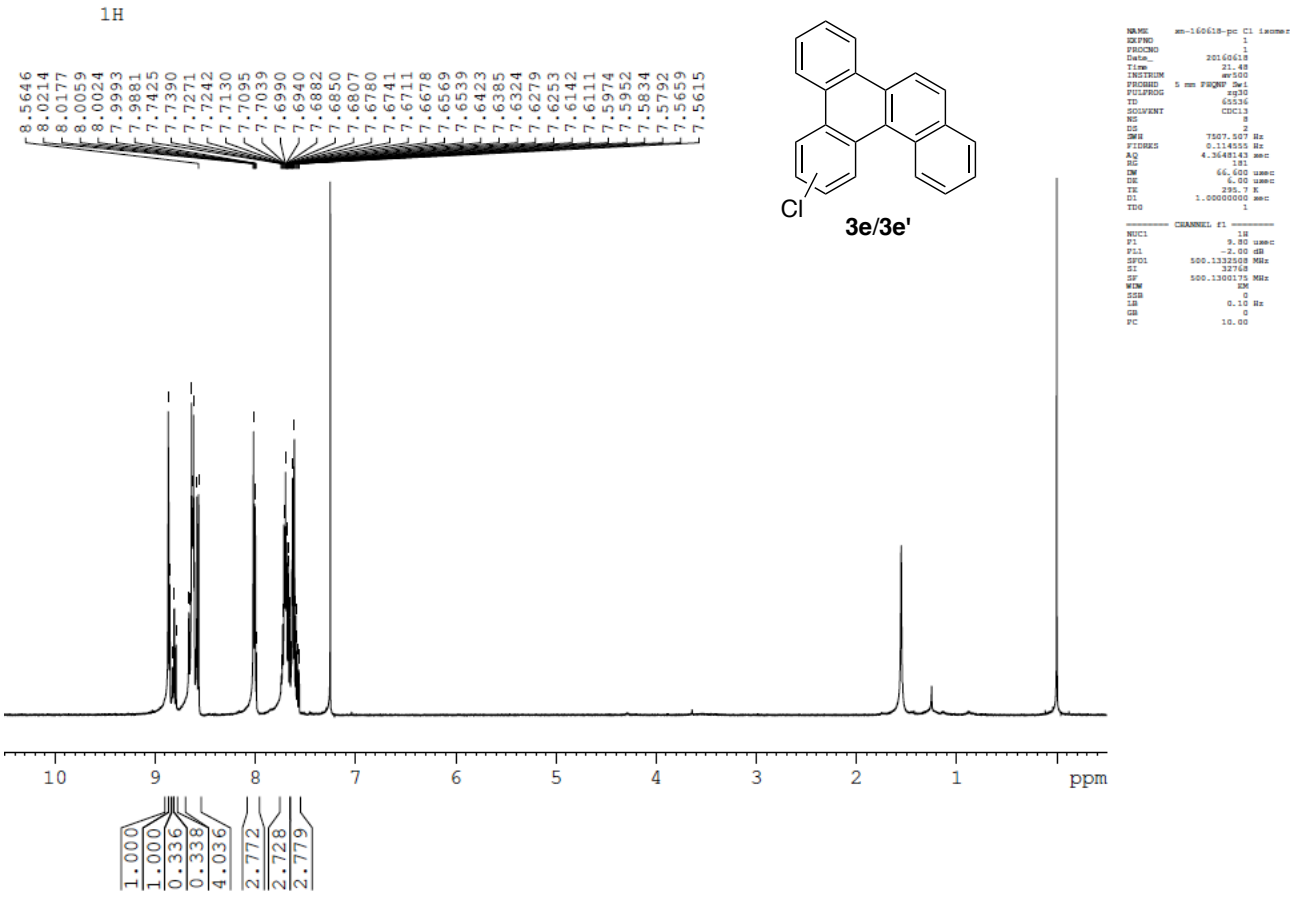


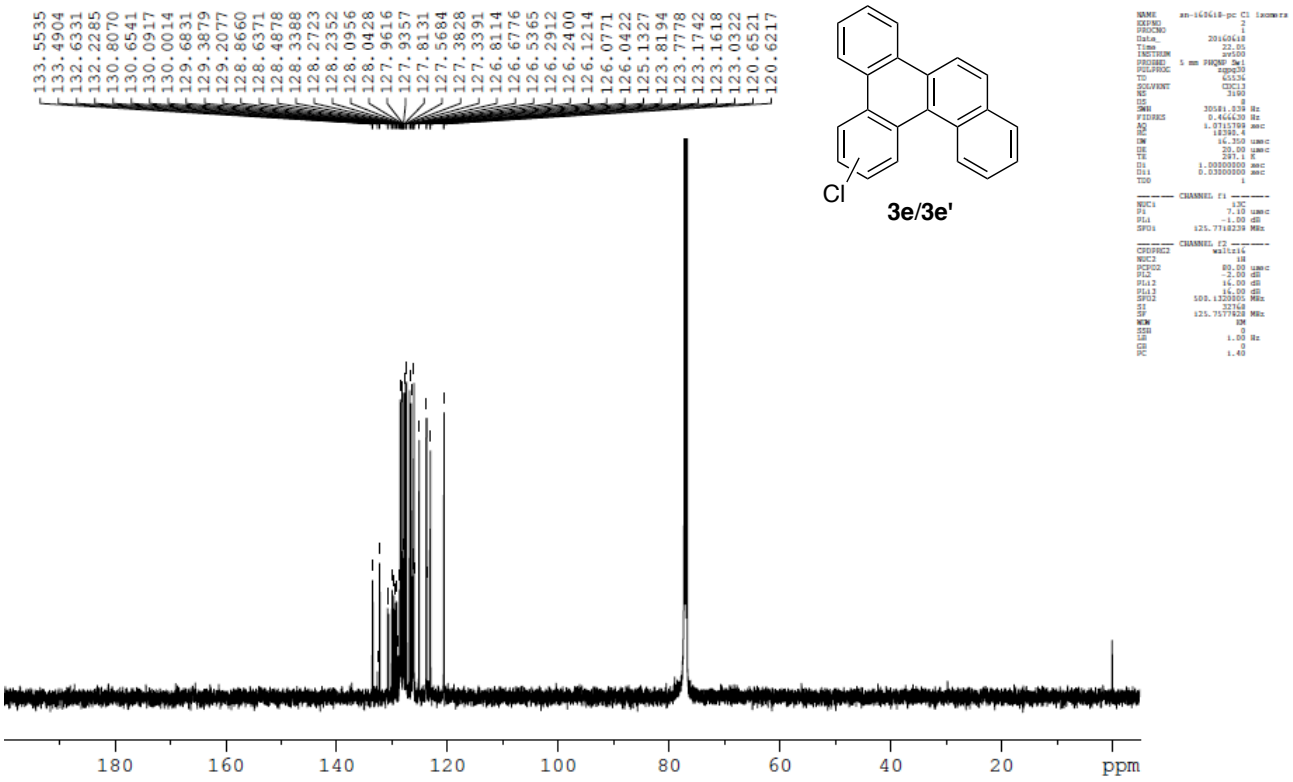
12-Methylbenzo[*g*]chrysene (3b) and 13-Methylbenzo[*g*]chrysene (3b')



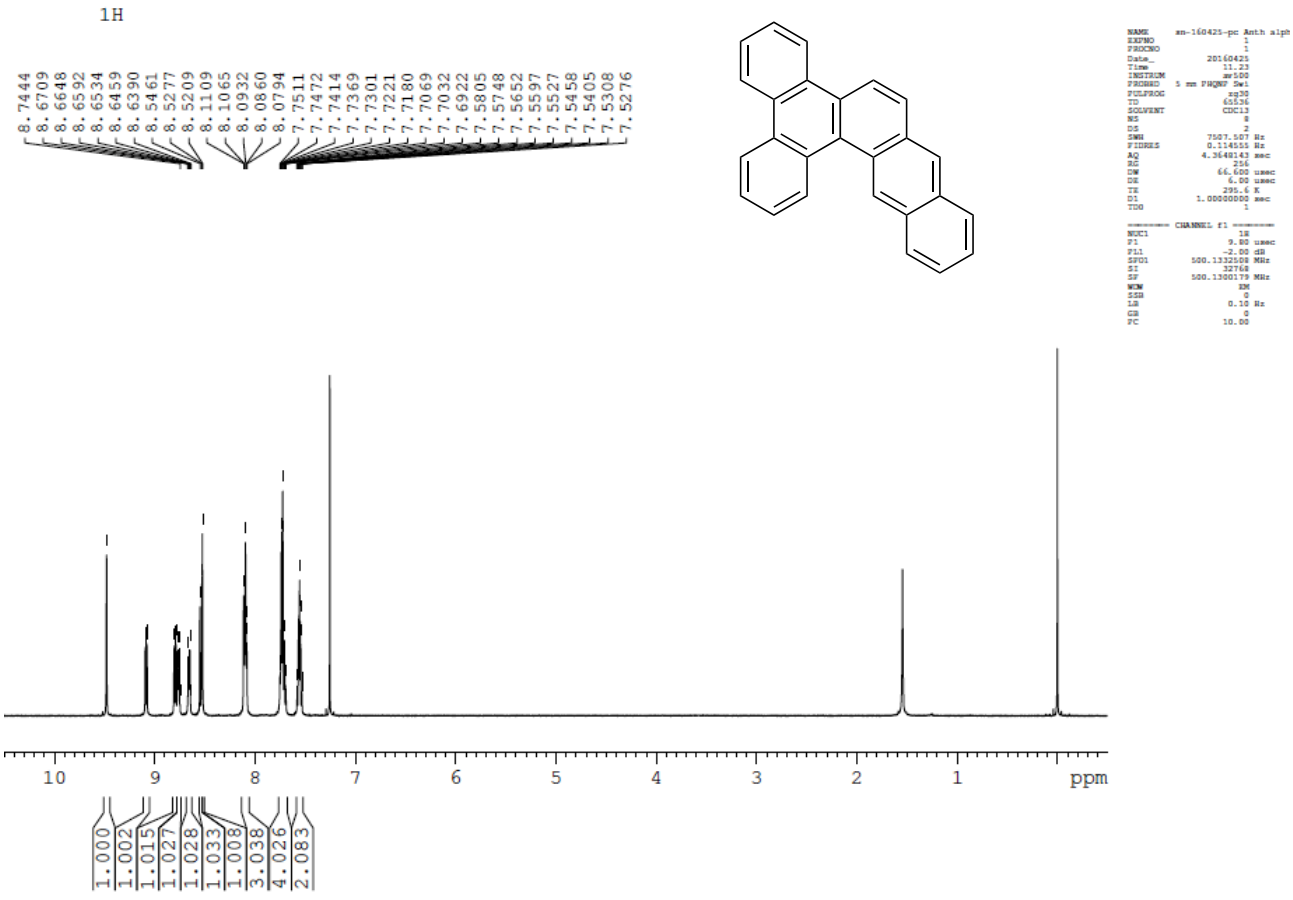


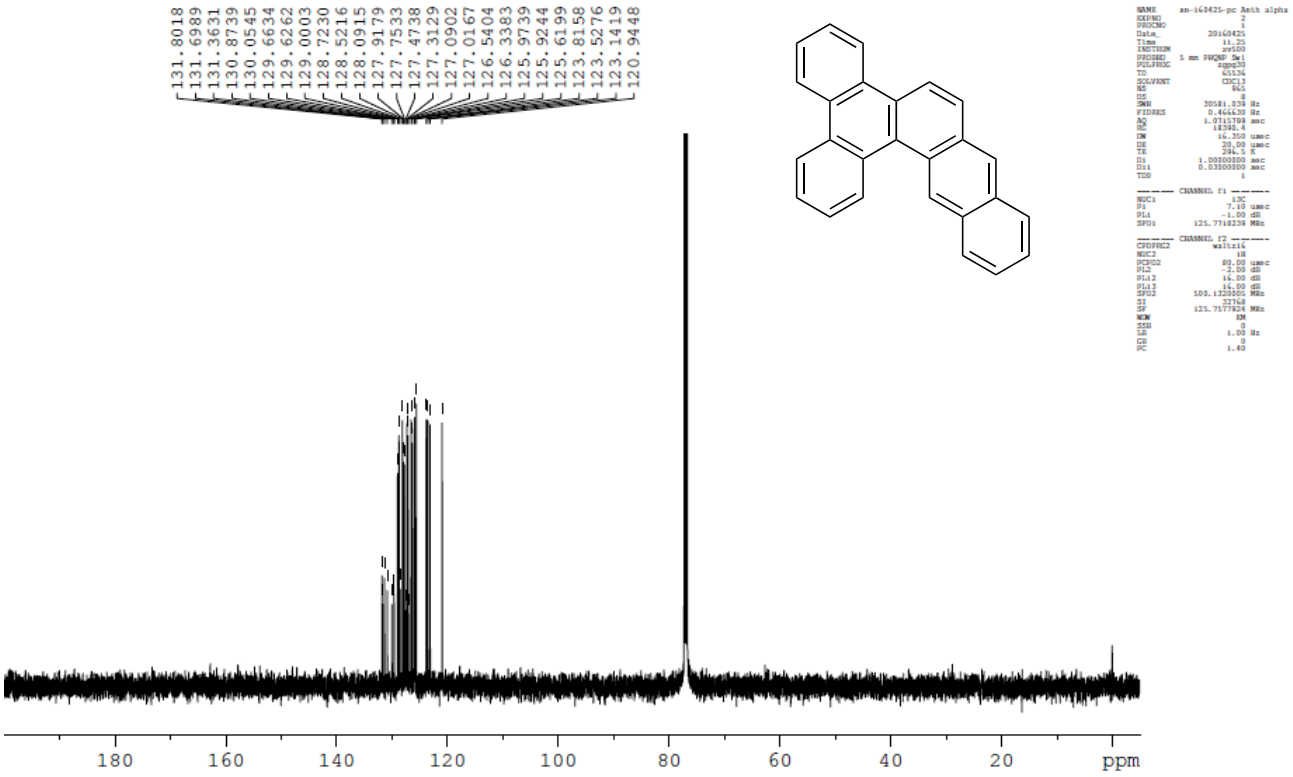
Chlorobenzo[*g*]chrysenes 3e and 3e'





Dibenzo[*a*,*c*]tetraphene (3g)

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